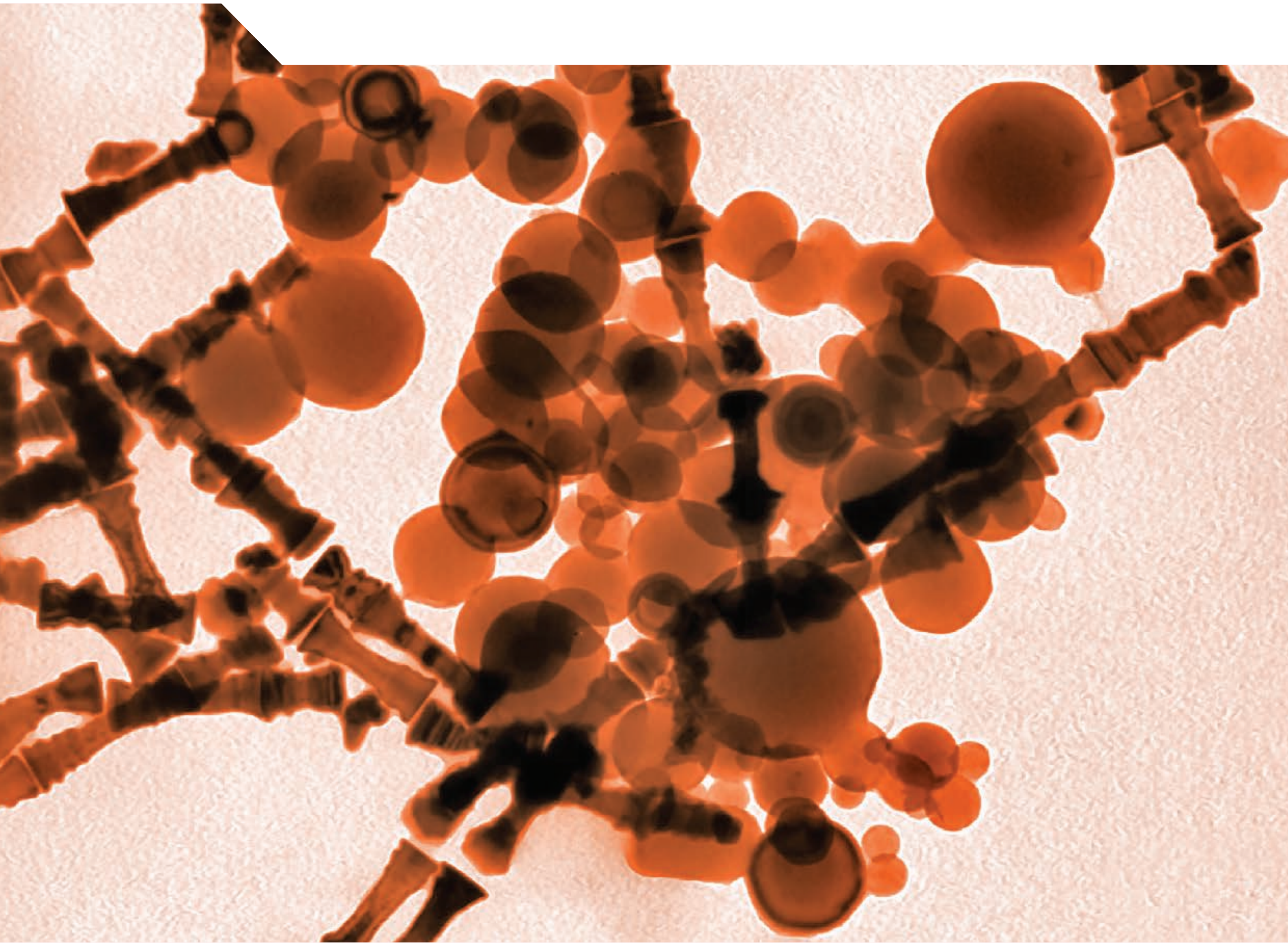
Nanomaterials in Waste Streams

CURRENT KNOWLEDGE ON RISKS AND IMPACTS



Nanomaterials in Waste Streams

CURRENT KNOWLEDGE ON RISKS AND IMPACTS

OECD
BETTER POLICIES FOR BETTER LIVES

This work is published under the responsibility of the Secretary-General of the OECD. The opinions expressed and arguments employed herein do not necessarily reflect the official views of OECD member countries.

This document and any map included herein are without prejudice to the status of or sovereignty over any territory, to the delimitation of international frontiers and boundaries and to the name of any territory, city or area.

Please cite this publication as:
OECD (2016), *Nanomaterials in Waste Streams: Current Knowledge on Risks and Impacts*, OECD Publishing, Paris.
http://dx.doi.org/10.1787/9789264249752-en

ISBN 978-92-64-24061-2 (print)
ISBN 978-92-64-24975-2 (PDF)

The statistical data for Israel are supplied by and under the responsibility of the relevant Israeli authorities. The use of such data by the OECD is without prejudice to the status of the Golan Heights, East Jerusalem and Israeli settlements in the West Bank under the terms of international law.

Photo credits: Cover © Georgy Shafeev/Shutterstock.com

Corrigenda to OECD publications may be found on line at: *www.oecd.org/about/publishing/corrigenda.htm*.

© OECD 2016

You can copy, download or print OECD content for your own use, and you can include excerpts from OECD publications, databases and multimedia products in your own documents, presentations, blogs, websites and teaching materials, provided that suitable acknowledgement of OECD as source and copyright owner is given. All requests for public or commercial use and translation rights should be submitted to *rights@oecd.org*. Requests for permission to photocopy portions of this material for public or commercial use shall be addressed directly to the Copyright Clearance Center (CCC) at *info@copyright.com* or the Centre français d'exploitation du droit de copie (CFC) at *contact@cfcopies.com*.

Preface

Improving the management of materials and sharply reducing the impact of waste are key elements in any strategy to halt the on-going erosion of environmental resilience. This means policies and approaches that encourage the sustainable use of materials and ensure human health and environmental protection. Any such policies need to adapt to the rapidly changing manufacturing environment associated with technological and process innovations. One such innovation is the increasingly widespread use of engineered nanomaterials.

Nanomaterials are increasingly used in a variety of widely available products such as sunscreen, cosmetics, antibacterial textiles, lithium ion batteries, glass coating and tennis rackets. Nanomaterials are utilised in a range of applications due to their significantly enhanced properties, enabled by their nano-scale structure. However, these special chemical and physical characteristics are also associated with possible risks to environmental health and safety. A relative blank spot in scientific understanding lies in the area of waste management. Waste containing these materials is currently managed along with conventional waste without sufficient knowledge of the associated risks and impacts on the environment.

This report aims to provide an overview of the current state of scientific insights in this area, as well as the knowledge gaps. It investigates the literature on the fate and possible impacts of nanomaterials in specific waste treatment processes, including recycling, incineration, landfilling and wastewater treatment processes. It also highlights key messages, future research areas and possible approaches to effectively support the sustainable management of nanomaterials.

The report draws on knowledge generated within the OECD and beyond. The development of the report has been led by the Working Party on Resource Productivity and Waste (WPRPW) in close collaboration with the Working Party on Manufactured Nanomaterials (WPMN). The science in this area is rapidly evolving and the OECD is planning to pursue its efforts in this area in close co-operation with other organisations at the international and national level, including governments, research institutes, and academic circles.

Simon Upton
Director
OECD Environment Directorate

Foreword

This publication has been developed by OECD's Environmental Policy Committee through its Working Party on Resource Productivity and Waste (WPRPW). The individual chapters on recycling, incineration, landfilling and wastewater treatment have been developed by technical experts from Switzerland, Germany, Canada and France. At the OECD Secretariat the project was co-ordinated by Peter Börkey and Shunta Yamaguchi under the supervision of Shardul Agrawala, Head of the Environment and Economy Integration Division.

This work was initiated to attract attention to the potential risks that are linked to the presence of nanomaterials in waste treatment processes. As a first step, a "Scoping Study on Nanowaste" was developed by Jeremy Allan in May 2012 followed by a workshop on "Safe Management of Nanowaste" held in Munich on 9th-11th May 2012. This workshop contributed to identifying the state of knowledge in this area and led to the development of four reports on specific waste treatment processes of recycling, incineration, landfilling and wastewater treatment, which are presented in this publication.

Along with these efforts, the Working Party on Manufactured Nanomaterials (WPMN) has been investigating the possible impacts of nanomaterials on health and the environment since 2006. In September 2013, the OECD issued a Council Recommendation which suggests that existing regulatory frameworks are generally applicable to address safety assessment of nanomaterials with some possible adjustment required to handle the specificities of nanomaterials. Nevertheless, the OECD Council Recommendation does not imply that current waste management processes and techniques are generally appropriate in addressing potential impacts of nanomaterials. Current waste treatment facilities are not typically designed to handle Waste Containing Nanomaterials (WCNMs), potentially leading to emissions into the environment and the exposure of people to these substances. Therefore, this publication aims to identify the status of knowledge in this area, the knowledge gaps, as well as the areas where further work should be conducted in priority.

Given that the research on nanomaterials is rapidly evolving, this publication aims to deliver a snapshot of the current knowledge on the risks and impacts of nanomaterials entering these waste streams. The current findings are a compilation of intermediate results which are likely to evolve as the science progresses.

The report has been prepared as a joint effort of WPRPW member countries. The OECD Secretariat led the work in finalising the publication and drafted the assessment and recommendations chapter and the executive summary. The individual chapters have been developed by the following authors:

Chapter 1 on assessment and recommendations was prepared by Peter Börkey and Shunta Yamaguchi of the OECD Secretariat.

Chapter 2 on recycling of waste containing nanomaterials was prepared by Mathias Tellenbach from Terra Consult Bern (Switzerland).

Chapter 3 on incineration of waste containing nanomaterials was prepared by Julia Vogel and Benjamin Wiechmann with contributions from Susann Krause, German Federal Environment Agency (UBA).

Chapter 4 on landfilling of waste containing nanomaterials was drafted by Martha King, Jacinthe Séguin and Ashley Hui of Environment Canada.

Chapter 5 on nanomaterials released into wastewater treatment sludge was drafted by Jean-Yves Bottero, research director at the CNRS (National Centre for Scientific Research in France) and director of Labex-SERENADE.

The report also benefitted from extensive comments from OECD's Working Party on Resource Productivity and Waste and the Working Party on Manufactured Nanomaterials, including the country delegations as well as industry, represented by the Business and Industry Advisory Council to the OECD. The OECD Secretariat would like to particularly thank Switzerland, Germany, Canada and France for their intellectual and financial contributions to the work.

Table of contents

Tables

Figures

Acronyms

Ag (nAg)	Silver (nano-Silver)
Ag_2S (nAg_2S)	Silver-Sulfide (nano-Silver-Sulfide)
Al (nAl)	Aluminium (nano-Aluminium)
Al_2O_3 (nAl_2O_3)	Aluminium-Oxide (nano-Aluminium-Oxide)
ANR	French National Research Agency (Agence Nationale de la Recherche)
BAT	Best Available Technology / Best Available Techniques
BAuA	German Federal Institute for Occupational Safety and Health (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin)
BEP	Best Environment Procedure
BREF	BAT Reference Document (EU)
BSI	British Standards Institution
C_{60}, C_{80}	Fullerenes
Ca (nCa)	Calcium (nano-Calcium)
$CaO/CaCO_3$ ($nCaO/ nCaCO_3$)	Calcium-Oxide (nano-Calcium-Oxide)
CB	Carbon Black
CDW	Construction and Demolition Waste
Ce(III)/Ce(IV)	Cerium
$Ce(III)PO_4$	Cerium Phosphate
CeO_2 ($nCeO_2$)	Cerium-Dioxide (nano-Cerium-Dioxide)
CNT	Carbon Nanotubes
Cu (nCu)	Copper (nano-Copper)
EC	Electrocoagulation
EEA	European Environment Agency
EIONET	European Environment Information and Observation Network
ELV	End of Life Vehicles
ENM	Engineered Nanomaterials, see also MNM
EPA / US EPA	United States Environment Protection Agency
ESAC	European Centre for the Validation of Alternative Methods Scientific Advisory Committee
ESM	Environmentally Sound Management
EU	European Union
EU FP7	European Union Seventh Framework Program (R+D)
EUROSTAT	Statistical Office of the European Communities
Fe (nFe)	Iron (nano-Iron)
FeO/Fe_2O_3 ($nFeO/nFe_2O_3$)	Iron-Oxides (nano-Iron-Oxides)
FOEN	Swiss Federal Office for the Environment
FOPH	Swiss Federal Office for Public Health
ILSI	International Life Sciences Institute

ISO	International Organization for Standardization
ITA-AAS	Institute for Technology Assessment-Austrian Academy of Sciences
JRC	Joint Research Centre of the EU in Ispra (Italy)
$LiFePO_4$ ($nLiFePO_4$)	Phosphate (nano-Phosphate)
Li-ion	Lithium-ion
Mg (nMg)	Magnesium (nano-Magnesium)
MNM	Manufactured Nanomaterials
MSW	Municipal Solid Waste
MSWI	Municipal Solid Waste Incinerator
MWCNT	Multi Wall Carbon Nanotubes
NEEPH	Nanomaterials Related Environmental Pollution And Health Hazards Throughout Their Life-Cycle (EU FP7)
NM	Nanomaterials
NP	Nanoparticles
NOM	Natural Organic Matter
PAH	Polycyclic Aromatic Hydrocarbons
PEN	The Project on Emerging Nanotechnologies
PET	Polyethylene Terephthalate
pH	Potential of Hydrogen
PPE	Personal Protective Equipment
PPC	Pollution Prevention and Control
Pt (nPt)	Platinum (nano-Platinum)
REACH	EU Regulation for Registration, Evaluation, Authorisation and Restriction of Chemicals
RCEP	United Kingdom Royal Commission on Environmental Pollution
RCRA	United States Resource Conservation and Recovery Act
ROS	Reactive Oxygen Species
SCENIHR	European Commission, Scientific Committee on Emerging and Newly Identified Health Risks
Se (nSe)	Selenium (nano-Selenium)
SECO	Swiss State Secretariat for Economic Affairs
SiO_2 ($nSiO_2$)	Silica, Silicium-Dioxide (nano-Silica)
SMM	Sustainable Materials Management
Sn (nSn)	Selenium (nano-Selenium)
SWCNT	Single Wall Carbon Nanotubes
TiN (nTiN)	Titanium-Nitride (nano-Titanium-Nitride)
TiO_2 ($nTiO_2$)	Titanium-dioxide (nano-Titanuim-Dioxide)
UV	Ultra Violet
VCI	German Chemical Industry Association (Verband der Chemischen Industrie e.V.)
WCNM	Waste Containing Nanomaterials
WEEE	Waste Electronic and Electrical Equipment
WPMN	Working Party on Manufactured Nanomaterials
WPRPW	Working Party on Resource Productivity and Waste
WWICS	Woodrow Wilson International Centre for Scholars
ZnO (nZnO)	Zinc-Oxide (nano-Zinc-Oxide)
Zr (nZr)	Zirconium (nano-Zirconium)

Executive summary

Engineered nanomaterials (ENMs), defined as in the scale of 1nm to 100nm, are increasingly utilised in applications of industrial, commercial and medical sectors bringing many benefits to society in the field of health and medical care, clothing, construction material, electronic and sporting equipment. Examples of products that contain ENMs are sunscreen, deodorant, water repellent and antibacterial textiles, lithium ion batteries, glass coating, and tennis rackets.

However, the potential risks and impacts of engineered nanomaterials to humans and the environment are currently insufficiently understood. Due to their size, shape, structure and distinctive properties, some potentially hazardous ENMs may be of concern to human beings, living organisms and ultimately to the environment. Although ENMs are very diverse and not all of them are potentially toxic, recent research shows that some nanomaterials may show cancer-causing properties in lungs, bypass important protective biological mechanisms such as the blood-brain barrier, or negatively affect the environment, for instance due to their antibacterial properties. Moreover, ENMs in some instances can increase the bioavailability, i.e. possible biological intake, of pollutants as a result of absorption and adsorption of other toxic particles.

Between 2006 and 2011, the number of products containing nanomaterials has been multiplied by 5 at the global level, and more than 1 300 products have been identified to contain them. The global market for nanomaterials is estimated at 11 million tonnes with a market value of EUR 20 billion in 2012. Accordingly, the turn-over with products that use nanotechnology is expected to increase from EUR 200 billion in 2009 to EUR 2 trillion by 2015. Despite these trends and the associated risks, waste containing nanomaterials (WCNMs) are currently disposed along with conventional waste without any special precautions or treatment. This raises the question as to whether existing waste treatment processes are able to effectively minimise the risks that may be linked to ENMs.

This report surveys the available evidence from the literature for four specific waste treatment processes: recycling, incineration, landfilling and wastewater treatment, and identifies the current state of knowledge on the fate and possible impacts of ENMs in these processes.

Key messages

Although state of the art waste treatment facilities have in some instances shown to retain or eliminate ENMs from the waste stream, there are still many areas that require further research due to the large number of different types of ENMs, the diversity of different waste treatment facilities and uncertainties about the actual composition of waste. This is the main conclusion that is drawn from the four literature surveys illustrated in the following chapters.

A lack of information on the types and quantities of ENMs in waste streams

The possible sources of ENMs entering different types of waste treatment facilities are fairly well identified, even if little is known about products and their content of ENMs or the quantities involved. ENMs can be collected from municipal waste for recycling in material recovery facilities or enter incineration plants as municipal solid waste or wastewater sewage sludge. They can also appear in wastewater treatment facilities through household drainage, commercial and industrial sewage or landfill leachate. Ultimately, ENMs can end up in landfills as contaminants in industrial and household waste along with ash and slag generated from incinerators or bio solids from wastewater treatment plants. An important knowledge gap is linked to a lack of information on the types and quantities of ENMs entering different waste streams.

While state of the art waste treatment processes may be able to retain a large share of ENMs, significant amounts of emissions are still likely to pass through them

Initial findings suggest that a large share of ENMs could be captured, diverted or eliminated by state of the art waste treatment processes, however with different levels of uncertainty. While a large amount of ENMs may be retained or eliminated by state of the art waste treatment processes, a significant share of ENMs may still be released as emissions, which is a cause for concern. Pilot wastewater treatment plants are able to capture and divert over 80% of ENMs by mass into solid sludge for some types of nanomaterials, while the rest would remain in the form of ENMs and be washed into surface water bodies. Similarly, incinerators with effective flue gas treatment systems, i.e. exhaust gas filters, may be able to capture a large share of ENMs and divert them into solid residuals such as fly and bottom ash. However these results are not well established for the moment as different studies find very different levels of removal efficiency. There is significantly less information available for landfilling and recycling operations. Moreover, initial research has only been able to draw findings for a few types of ENMs for each waste treatment process, and many of the results stem from laboratory testing or modelling. Therefore the fate of ENMs in these waste treatment plants still comprises of a level of uncertainty.

Best available technologies currently appear most effective in minimising risks

Under these circumstances, where the fate, impacts and risks of ENMs are still relatively uncertain, the application of best available technologies (BAT) in waste treatment facilities, although they are not specifically designed to address ENMs, appear to be a pragmatic approach to minimising risks linked to ENMs in waste flows.

As a consequence, there are serious concerns about the effectiveness of waste treatment processes that use sub-standard technologies, such as incinerators with insufficient flue gas treatment or uncontrolled landfills. These technologies are still widespread in many parts of the world and, while virtually nothing is currently known about their effectiveness in retaining ENMs, it must be assumed that their ability to contain these risks is very limited.

There are particular concerns with the treatment of residual waste, where very little is known to date

Even if state of the art waste treatment processes may successfully capture, divert or eliminate ENMs, there are concerns that subsequent steps of treating residual wastes and/

or material recovery may lead to their release into the environment. The most alarming case is perhaps the agricultural application of wastewater sludge. The potential transformation of ENMs in soil, their interactions with plants and bacteria in the rhizosphere, and their transfer to surface water has never been studied in depth. Another case of concern is that ENMs can be collected as residual ashes such as fly ash and bottom ash in incinerators or solid sludge in wastewater treatment plants and transferred to landfills for final disposal where the fate of ENMs is still unknown. In addition, there are also potential concerns over secondary materials produced from recycling processes which can be contaminated with ENMs.

Furthermore ENMs can have negative effects on certain waste treatment processes themselves

ENMs may also have negative effects on the waste treatment processes itself. Surface functionalised nanomaterials, may slow down the transformation kinetics of nanomaterials in wastewater treatment plants and may have negative effects on the entire process. Similarly, certain organic substances present in landfill leachate could lead to stabilise ENMs and potentially result in lowered performance of leachate treatment. Moreover, ENMs may inhibit specific processes that prevent pollutants and excess nutrients from leaching into the environment known as anaerobic or denitrification processes in wastewater treatment facilities, and this behaviour may ultimately deteriorate the plant’s capacity to reduce toxicity in sludge.

Future research areas and possible approaches

As a consequence, the following areas for further research are recommended given the importance of these topics and the absence of sufficient knowledge in the literature review:

Identification and quantification of ENMs in waste flows

- Identify the types and quantities of ENMs entering waste treatment processes.

Behaviour and fate of nanomaterials in waste treatment processes

- Assess the effectiveness of real scale operations such as actual plants or pilot plants incorporating all stages of waste treatment processes and using actual waste products.
- Deepen the understanding of the fate of ENMs in waste treatment processes, particularly in the following areas:
  - Where scientific findings are currently contradictory (anaerobic and denitrification processes of wastewater treatment, flue gas treatment of incinerators).
  - Where there is an insufficient number of studies available (recycling facilities, landfills).

Potential emissions of ENMs from residual waste and/or material recovery

- Investigate the impact of agricultural application of sludge containing ENMs.
- Investigate the effectiveness of landfills in serving as a final sink for ENMs.
- Investigate potential risks of secondary materials that contain ENMs.

Emission control and Best Available Technologies

- Determine the effectiveness of best available waste treatment technologies in retaining or eliminating ENMs and protecting workers from exposure to ENMs.
- Assess the effectiveness of sub-standard waste treatment technologies (e.g. incinerators with inadequate flue gas treatment, clay liners in older landfills or uncontrolled landfills).
- Research other measures to effectively capture, divert or eliminate ENMs from waste streams and residual waste.

Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 1

Assessment and recommendations

This overview chapter highlights the findings from subsequent chapters that focus on four specific waste treatment processes: recycling, incineration, landfilling, and wastewater treatment. The chapter clarifies the current state of knowledge on the fate and possible impacts of nanomaterials in these processes, provides possible ways forward and identifies future research areas and possible approaches to further address the emerging issue of waste containing nanomaterials.

Nanotechnologies are increasingly utilised in advanced applications of industrial, commercial and medical sectors bringing many benefits to society (Brar et al., 2010). However, their potential risks and impacts to human beings and the environment are currently insufficiently understood and under investigation. Nanomaterials, defined as materials of which a single unit are sized between 1 to 100nm, have distinctive features which can benefit various applications from health and medical care, clothing, electronic equipment, construction material and sporting equipment (PEN, 2013). For example, some nanomaterials can be utilised in sunscreen for its properties of shielding Ultra Violet (UV) light, while other nanomaterials have anti-bacterial features useful for deodorant and textiles. Certain nanomaterials can be used in lithium ion batteries to extend their product life while other types of nanomaterials can be applied to building material and glass coating to retain self-cleaning features. Nanomaterials are also used in tennis rackets to achieve lightweight performance and durability.

The number of products containing nanomaterials has increased by 521% from 2006 to 2011 reaching over 1 317 products according to the Woodrow Wilson International Centre for Scholars (WWICS) Nanotechnology Consumer Products Inventory (WWICS, 2011). In 2012, the global market for nanomaterials was evaluated at 11 million tonnes with a market value of EUR 20 billion. Accordingly, products underpinned by nanotechnology are expected to grow from EUR 200 billion in 2009 to EUR 2 trillion by 2015. (EU, 2015, 2012).

However, due to their size, shape, structure and distinctive properties, recent research indicates that some nanomaterials may represent a risk to human health, living organisms and the environment. For example, some nanomaterials may potentially show cancer-causing properties in lungs while other nanomaterials with antibacterial properties may potentially harm ecosystems when they reach the environment (Struwe et al., 2012). Moreover, some nanomaterials are able to bypass important protective biological mechanisms such as the blood-brain barrier, which may produce adverse effects related to neurotoxicity (Australia, Department of Health, 2013). Nanomaterials, in some instances, can also increase the bioavailability of pollutants as a result of absorption and adsorption of toxic particles (Farré et al., 2009; He et al., 2012; Gao et al., 2008; Cheng et al., 2004; Yang et al., 2006).

The assessment of exposure to nanomaterials in the environment is identified as a significant issue (Gottschalk and Nowack, 2011), even though it is sometimes challenging to distinguish engineered nanomaterials (ENMs), which are designed and manufactured for specific purposes, from naturally occurring nanomaterials such as metallic silver nanomaterials naturally produced by UV radiation or metallic mercury naturally formed under anoxic conditions (von der Kammer et al., 2014).

This publication focuses on engineered nanomaterials as defined by the International Organization for Standardization (ISO) (see Box 1.1) and it focuses on these materials to the extent that they are contained in different waste streams, which in the following will be termed "waste containing nanomaterials" (WCNM). The term "nanowaste", which is also sometimes encountered in the literature, should only be used for specific waste containing high levels of nanomaterials generated by nanomaterial production, i.e. in an industrial context.

Box 1.1. **Definitions of nanomaterials**

Nanoscale:	Size range from approximately 1 to 100 nm.
Nanomaterial:	Material with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. This generic term is inclusive of nano-object and nanostructured material.
Nano-object:	Material with one, two or three external dimensions in the nanoscale.
Nanostructured material:	Material having internal nanostructure or surface nanostructure.
Nanostructure:	Composition of inter-related constituent parts, in which one or more of those parts is a nanoscale region.
Engineered nanomaterial:	Nanomaterial designed for a specific purpose or function

Note: Engineered nanomaterials (ENMs) and manufactured nanomaterials (MNMs) are used synonymously in various research documents however we will align to ENMs in this documentation for the purpose to align with ISO standards.

Source: ISO/TS 80004-1:2015 and ISO/TS 12901-1:2012

What is the link to waste management?

With increasing industrial and commercial applications of nanomaterials, it can be asserted that more nanomaterials are entering waste streams and could subsequently affect end-of-life disposal processes (NEEPH, 2011).

The purpose of waste management is either to recycle waste materials to produce secondary raw materials or to dispose of waste materials, by landfilling, incinerating or storing them in an adequate manner. End-of-life products containing nanomaterials are part of the main solid municipal waste stream and thus subject to four different treatment pathways:

1. *Recycling facilities*

   There are generally several stages in the recycling process. For example, synthetic materials and metals are shredded in order to homogenise the size of waste particles or separate out unwanted materials. Particles can be released and dust containing nanoparticles can be created. For work safety reasons these processes already take place under specific conditions that prevent such dust from coming into contact with human beings or the environment.

2. *Incineration facilities*

   Waste is mixed and thermally treated in incineration plants. Combustible parts are destroyed and residues leave the combustion chamber either as slag or as dust in the flue gas. Modern flue gas filter and cleaning facilities reduce the amount of hazardous substances to the detectable minimum. However, very little information exists about the efficiency of cleaning in respect to nanomaterials. In the worst case the particles are not collected or destroyed and leave the chimney unfiltered into the environment.

3. *Landfilling facilities*

   Landfilling of untreated (biodegradable, combustible) waste is still the major waste management technique in many countries. Depending on how and where landfilling is organised and practised, nanomaterials may leave the landfill by emission into air, water, and possibly soil.

4. *Wastewater treatment facilities*

   Products containing nanomaterials can release nanomaterials during their use-phase and in contact with water. This is the case for example when textiles are washed in a washing machine or from surface coatings. As a result, nanomaterials can be found in waste waters and thus in the sewage sludge of waste water treatment plants which may be incinerated or used as a fertiliser in agriculture. A lack of knowledge exists on environmental impacts resulting from the use of sewage sludge in agriculture.

To what extent are increasing amounts of ENMs in waste streams retained or eliminated by different waste treatment processes and what is their impact on the effectiveness of these processes? This is the main question that is posed to this research. To this end, this publication provides a literature review of the four specific waste treatment processes of recycling, incineration, landfilling, and wastewater treatment. It aims to clarify the current state of knowledge on the fate and possible impacts of ENMs in these processes.

This section will first summarise the current state of knowledge on the fate of WCNMs in waste treatment processes based on the insights provided in the four subsequent chapters and then identify some possible ways forward. Following this overview, a study on the fate and possible impact of nanomaterials in recycling facilities is provided in Chapter 2, a study on the current information of WCNMs in incineration processes in Chapter 3, an investigation on the possible impacts of WCNMs in landfills in Chapter 4, and an examination on WCNMs in wastewater treatment processes in Chapter 5.

What is the current state of knowledge on the fate of WCNMs in waste treatment facilities?

Although state of the art waste treatment facilities are likely to collect, divert or eliminate a large share of nanomaterials from these waste streams, there is still a fair amount of uncertainty associated with their final disposal, requiring more research in this area. This is the main conclusion that is drawn from the four literature surveys illustrated in the following chapters. The possible sources of WCNMs and the interconnections between these waste treatment processes are fairly well identified. However, the types and quantities of ENMs entering these waste streams are still largely unknown. Moreover, the available studies on the fate and possible impact of ENMs in waste treatment processes provides a mixed picture, with certain types of ENMs relatively more researched, for example nano-silver (nAg), nano-titanuim oxide ($nTiO_2$), nano-zinc oxide (ZnO), nano-cerium oxide ($nCeO_2$) and carbon nanotubes (CNTs). On the other hand, others lack information, for example metals such as nano-iron (nFe), nano-aluminium (nAl), nano-platinum (nPt), or nano-zirconium (nZr), metal oxides such as nano-silica ($nSiO_2$), or nanoclay. In general, research is not sufficiently developed to draw concrete conclusions at this point.

What are the types and quantities of ENMs in waste streams?

The possible sources of ENMs entering waste treatment facilities are fairly well identified among the four typical treatment processes of recycling, incineration, landfilling and wastewater treatment even if little is known about which products contain ENMs and which ENMs these are. ENMs can be in forms of pure nanomaterials, items contaminated with nanomaterials, liquid suspensions containing nanomaterials or solids which have friable nanomaterials (BSI, 2007), and they could be potentially released through mass production of ENMs, distribution, consumption and final disposal of products containing ENMs (NEEPH, 2011). They can be collected to recycling facilities as a part of municipal solid waste and end-of-life products. They can also enter incineration plants as municipal solid waste or wastewater sewage sludge (Asmatulu et al., 2012; Boldrin et al., 2014; Ganzleben et al., 2011; Keller A.A. et al., 2013; Reinhart et al., 2010; Nowack et al., 2013), or appear in waste water treatment facilities through household drainage, commercial and industrial sewage or landfill leachate (Auffan et al., 2010a, 2010b; Musee, 2011; Kiser et al., 2009; Westerhoff et al., 2011). Ultimately, they can end up in landfills as contaminants in industrial and household waste along with ash and slag generated from incinerators or bio solids from wastewater treatment plants (DiSalvo et al., 2008; Mueller et al., 2012).

These possible sources are compiled in Table 1.1.

Table 1.1. **Possible sources of WCNMs**

Waste treatment processes	Possible sources of ENMs
Recycling facilities	● Municipal solid waste ● End-of-life products
Incineration plants	● Municipal solid waste ● Sludge and bio solids from wastewater treatment plants
Landfills	● Municipal solid waste ● Fly ash and bottom ash from incinerators ● Sludge and bio solids from wastewater treatment plants
Wastewater treatment facilities	● Household drainage ● Commercial and industrial sewage ● Landfill leachate

However, the types and quantities of ENMs entering these waste streams are still unidentified to date (Health Council of the Netherlands, 2011). Given that there is a significant increase in products containing ENMs and that eventually need to be disposed of, it is anticipated that more and more ENMs are entering these waste streams. The waste treatment processes can be potentially affected according to the types and/or volumes of ENMs and therefore the identification and quantification of flows of ENMs has been recognised as one of the priority issues from all four chapters of recycling, incineration, landfilling, and wastewater treatment.

Are ENMs being captured in waste treatment processes?

Initial findings suggest that a large share of ENMs could be captured, diverted or eliminated by state of the art waste treatment processes, however with different levels of uncertainty. While a large amount of ENMs may be retained or eliminated by state of the art waste treatment processes, a significant share of ENMs may still be released as emissions, which is a cause for concern.

Municipal wastewater treatment has been investigated for some types of nanomaterials such as nano-titanuim oxide ($nTiO_2$), nano-silver (nAg), nano-cerium oxide ($nCeO_2$) or nano-copper (nCu). Pilot wastewater treatment plants were able to capture and divert over 80% of ENMs by mass into solid sludge in its aerobic processes through transformation, bacterial aggregation, biological polymer adsorption and sedimentation (Kiser et al., 2009 and 2010; Kaegi et al., 2011; Ganesh et al., 2010; Wang et al., 2012; Gomez-Rivera et al., 2012). As a result, the residuals would remain in the form of ENMs and appear in surface water (Tiede et al., 2010; Kim et al., 2010).

Other studies focused on waste incinerators and found that state-of-the-art flue gas treatment systems could capture a significant share of ENMs diverting them into fly ash and bottom ash. However, the removal efficiency of ENMs was reported differently across several studies. Some studies suggest that electrostatic precipitators and wet flue gas purification systems effectively remove most ENMs from emissions in the case of nano-cerium dioxide ($nCeO_2$) (Walser et al., 2012), whereas other studies conclude that up to 20% could pass through these systems requiring additional preventive mechanisms to retain these (Roes et al., 2012).

There is significantly less information available for landfilling operations. Based on the results of municipal wastewater treatment studies, it is suspected that the treatment processes for landfill leachate may display similar levels of effectiveness in capturing ENMs through aggregation and agglomeration with organic matter and bacteria (Bottero et al., 2015; Kaegi et al., 2011; Westerhoff et al., 2013). However, leachate is an aqueous effluent that is quite different from municipal wastewater and more specific studies would be required to confirm this expectation. Only very few studies investigate the effectiveness of landfill liners in retaining ENMs from leaching to the environment and initial findings are contradictory where they are available (Boylard et al., 2013; Lozano and Berge, 2012; Siddique, 2013). Moreover, the extent to which the landfill surface or landfill gas can release ENMs to the environment has never been studied in depth.

Finally, the fate of nanomaterials in recycling processes, including dismantling, shredding and thermal processes is unclear because of challenges in ENM exposure measurement in actual working environments (Gottschalk and Nowack, 2011). Therefore, these studies have largely relied on modelling results.

In general, initial research has only been able to draw findings for a few types of ENMs and many studies have relied on laboratory experiments or modelling results, rather than investigating existing facilities. The fate of ENMs in different waste treatment plants, therefore, still comprises of a level of uncertainty and requires further investigation.

Can ENMs negatively affect leachate and wastewater treatment processes?

Beyond concerns relating to the capacity of waste treatment operations in retaining ENMs, there are also questions as to whether ENMs could have negative effects on the waste treatment processes itself. For instance, surface functionalised nanomaterials, which are relatively stable with limited aggregation and sedimentation levels in the aerobic processes, may slow down the transformation kinetics of nanomaterials in wastewater treatment plants and negatively affect the entire process (Auffan et al., 2010a; Barton et al., 2013; Kiser et al., 2010).

Furthermore, research suggests that certain ENMs may also inhibit anaerobic or denitrification processes in municipal wastewater treatment facilities. It is reported that

ENMs with metallic properties at high concentrations may inhibit the anaerobic or denitrification process with impact on bacterial communities and ultimately deteriorate the plant's capacity to reduce toxicity in sludge (Arnaout and Gunsch, 2012; Holden et al., 2014; Kiser et al., 2010; Klaine et al., 2008; Nguyen, 2013; Yang et al. 2013). Better information on the types and quantities of ENMs entering these processes could help to anticipate the potential risks.

Similarly, organics such as humic and fluvic acid in leachate could also stabilise ENMs minimising aggregation and reducing precipitation potentially leading to poor performance of leachate treatment facilities (Hyung and Kim, 2008; Saleh et al., 2010; Lin and Xing, 2008).

What are the issues raised by the linkages of waste treatment processes and residual waste?

Even though there is some evidence that state of the art waste treatment processes may successfully capture, divert or eliminate ENMs from waste streams into solid sludge in wastewater treatment processes or fly ash and bottom ash in incineration processes, there are concerns that subsequent steps of treating the residual wastes and/or material recovery may lead to potential releases into the environment.

The most alarming case is perhaps the agricultural application of wastewater sludge. According to a study from France, more than half of the country's wastewater sludge is currently used for soil fertilisation in agriculture (ADEME, 2004). Given that increasing amounts of ENMs are entering wastewater treatment processes, there is a risk that more and more ENMs are contained in wastewater sludge. The potential transformation of ENMs in soil, their interactions with plants and bacteria in the rhizosphere, and their transfer to surface water has never been studied in depth, and the ultimate fate of ENMs disposed of in this way therefore remains a major area of uncertainty.

Similarly, the relatively limited knowledge of the fate of ENMs in landfills is another cause of concern as these are typically the final sinks where residual waste from incineration and wastewater treatment will be disposed of. Incinerators collect ENMs through their filters, accumulate them as fly ash and bottom ash, which is then sent to landfills for final disposal (Mueller et al., 2013). Similarly, solid sludge from wastewater treatment may be sent to landfills in some occasions (DiSalvo et al., 2008; Lui et al., 2014; Westerhoff et al., 2013).

Further issues may arise when material is recovered from the waste stream for the use in different applications, as secondary materials may be contaminated with ENMs and their potential risks are largely unknown (Chaudhry et al., 2009). This includes cases of industrial application of incinerator fly and bottom ash, for instance in road construction. The possible leakage routes from waste treatment operations are summarised in Table 1.2.

Table 1.2. **Possible leakage routes of ENMs from waste treatment operations**

Waste treatment processes	Possible leakage routes
Recycling	● Imbedded in secondary materials
Incineration	● Flue gas emissions to the environment ● Fly ash and bottom ash to landfills ● Fly ash and bottom ash to storage facilities ● Bottom ash to industrial applications (e.g. roads)
Landfilling	● Landfill gas emissions to the environment ● Landfill surface emissions to the environment ● Leachate to leachate treatment facilities ● Leachate to wastewater treatment facilities
Wastewater treatment	● Emissions to surface water ● Wastewater sludge to incinerators ● Wastewater sludge to landfills ● Wastewater sludge to agriculture applications

How much do we know about the best ways to manage the risks identified so far?

In a context where the fate, impacts and risks of ENMs are still relatively uncertain, a number of studies suggest that the application of best available technologies may constitute a pragmatic approach in dealing with these potential risks and the related uncertainty (Boeni, 2013; Japan Ministry of Environment, 2009; NEEPH, 2011; SRU, 2011; Struwe et al., 2012). Although best available technologies (BAT) are not typically designed to deal with ENMs (OECD, 2004/2007; EU, 2008), their use may be an effective way of minimising exposure. For example, in the case of Europe, the application of BAT for incineration flue gas treatment is seen to be more effective than conventional technologies in scrubbing ENMs from flue gas. Similarly, it is perceived that modern engineered landfills are better able to prevent releases of ENMs than un-engineered landfills.

In recycling facilities, where workers may be exposed to ENMs through shredding, thermal and dismantling processes, workers could be protected through a range of safety measures such as:

1. technical measures (minimising dust through sealing, extracting, filtering, isolation and ventilation, use of wiping by damp cloth altering blowing etc.),
2. organisational measures (minimise exposure time, minimisation on persons exposed, restriction of access and instructions of personnel on hazards and protection measures), and
3. personal measures (respiratory protection with particle filters, protection gloves, closed goggles, protection suit etc.) (Struwe et al., 2012).

As a consequence, the potential risks emanating from ENMs in different waste treatment facilities are probably significantly larger in sub-standard operations, of which many are still in operation around the globe and which are predominant in less developed parts of the world. This is an area where further research is urgently needed.

The current state of knowledge and knowledge gaps of the fate of ENMs in waste treatment processes are compiled in Table 1.3.

What is the possible way forward?

The four chapters of this book show that while there has been some research into different aspects of wastes containing nanomaterials, this is insufficient to be conclusive

Table 1.3. **Current state of knowledge and knowledge gaps of the fate of ENMs in waste treatment processes**

Key Issues	Recycling	Incineration	Landfilling	Wastewater treatment
Identifying possible sources	● The possible sources of ENMs entering waste treatment facilities are fairly identified ● Information on types and quantities of ENMs entering these waste streams need to be clarified			
Capturing ENMs in waste treatment processes	● Fate of nanomaterials in recycling processes is unknown ● Challenge in measuring the exposure of ENMs in actual working environments. ● Available studies largely relied on modelling results.	● Incinerators with effective flue gas treatment systems are likely to capture a majority of ENMs and divert them to fly ash or bottom ash. The effectiveness however differs according to different studies.	● Landfill design, site conditions, and sophistication of control measures including landfill gas recovery, leachate collection and treatment systems heavily influence the release of contaminants through landfill gas and leachate. ● It is anticipated from wastewater treatment studies that leachate treatment would be effective in capturing ENMs. ● There is a lack of conclusive findings to determine whether ENMs penetrate or migrate through landfill liners. ● Further research on the release of ENMs from landfill surface or landfill gas to the environment is needed.	● For few nanomaterials (TiO2, Ag, CeO2, Cu) pilot wastewater treatment plants were able to capture and divert over 80% of injected ENMs by mass into solid sludge in aerobic process. ● Relatively small amount of residuals would appear in surface water.
Potential negative effects of ENMs on waste treatment processes	● Exposure in working conditions and to the environment is of concern.	● Unidentified	● Organics (e.g. humic and fluvic acid) in leachate could stabilise ENMs, which reduces particle aggregation (generally associated with greater material mobility) and potentially affect the performance of leachate treatment. ● ENMs may have the potential to inhibit microbial processes of landfill leachate treatment at high concentrations.	● Surface functionalised nanomaterials may slow down sedimentation and precipitation processes of ENMs in wastewater treatment plants. ● ENMs at high concentrations may inhibit the anaerobic or denitrification process and deteriorate the plants ability to reduce toxicity in sludge.
Linkages between waste treatment processes and residual waste	● Possibly imbedded in secondary materials. ● Growing interest in the recycling industry to recover material from bottom ash.	● Incinerators can collect ENMs through filters and accumulate them as fly ash or bottom ash, however, they may lead to landfills where more investigation is necessary. ● Fate of ENMs in solid residuals need further research (e.g. case of road application in Germany).	● Potential pathway to the environment if ENMs pass through landfill liners and leachate treatment. Secondary pathways could include landfill surface and landfill gas.	● Wastewater sludge can be transferred to agricultural applications. Potential transformation of ENMs in soil, their interactions with plants and bacteria in the rhizosphere, and their transfer to surface water has never been studied in depth.
Available measures for risk minimisation	● Best available techniques (BAT) do not typically address specific measures for ENMs, however may be a good approach to minimise exposure.			

and significant additional research is going to be needed, building-up to an almost overwhelming research agenda. The lack of knowledge and data is due to the fact that this is an emerging and active area of research in which new publications are constantly being released. However, the material also provides some indication on how work could be prioritised. Some of these suggestions are relatively straightforward and typically apply to the assessment of chemicals, such as to focus attention on high volume and high risk ENMs. The OECD's Working Party on Manufactured Nanomaterials is currently looking into assessing the hazard and exposure of different types of ENMs and should be able to provide important guidance in this respect. Similarly, it is suggested that research should focus on those ENMs that are contained in gases and liquids first, since the exposure to these is potentially greater than to solids, due to the fact that they spread more quickly and more easily enter the human body through inhaling or ingestion.

Research is also too often carried-out in the laboratory rather than using real products containing ENMs in actual waste treatment facilities. More needs to be done to assess the effectiveness of existing facilities, including those that do not operate according to best available technology standards, which are widespread in some parts of the world where most waste is treated in such operations.

The survey also suggests that, due to the linkages that exist between different waste treatment operations, there should be particular attention brought to those treatment technologies that are used to deal with residual wastes. Landfills are potentially going to receive the largest concentrations of ENMs as is suggested by the accumulation of ENMs in fly and bottom ash from incinerators as well as sewage sludge, all of which are frequently disposed of in landfills. Similarly, little attention has been brought to the use of sewage sludge that contains ENMs in agriculture or the risks that may be linked to ENMs that are contained in recycled materials.

Finally, there are a number of areas where the scientific evidence is currently contradictory, such as for anaerobic and denitrification processes in wastewater treatment, or where an insufficient body of research is available, such as for landfills and where more research is urgently needed.

Recommended areas for further research on waste containing nanomaterials

Recommended areas that require further research identified by the literature review are provided below.

Identification and quantification of ENMs in waste flows

- Identify the types and quantities of ENMs entering waste treatment processes.

Behaviour and fate of nanomaterials in waste treatment processes

- Assess the effectiveness of real scale operations such as actual plants or pilot plants incorporating all stages of waste treatment processes and using actual waste products.
- Deepen the understanding of the fate of ENMs in waste treatment processes in the following areas in particular:
  - Where scientific findings are currently contradictory (anaerobic and denitrification processes of wastewater treatment, flue gas treatment of incinerators).
  - Where there is an insufficient number of studies available (recycling facilities, landfills).

Potential emissions of ENMs from residual waste and/or material recovery

- Investigate the impact of agricultural application of sludge containing ENMs.
- Investigate the effectiveness of landfills in serving as a final sink for ENMs.
- Investigate potential risks of secondary materials that contain ENMs.

Emission control and Best Available Technologies

- Determine the effectiveness of best available waste treatment technologies in retaining or eliminating ENMs and protecting workers from exposure to ENMs.
- Assess effectiveness or impacts of sub-standard waste treatment technologies (e.g. incinerators with inadequate flue gas treatment, clay liners in older landfills or uncontrolled landfills).
- Research effective measures to capture, divert or eliminate ENMs from waste streams and residual waste.

References

ADEME (2004), "Production and management of sewage treatment plant sludge in France (2000-04)", Syntheses related to the production and management of sludge from wastewater treatment plants in France, *http://paysdefayence.free.fr/epuration-eaux/boues_STEP_synthese.pdf*.

Arnaout C.L. and C.K. Gunsch (2012), "Impacts of Silver Nanoparticle Coating on the Nitrification Potential of Nitrosomonas Europaea", *Environmental Science & Technology*, Vol. 46, pp. 5387-5395.

Asmatulu, E. et al. (2012), "Life cycle and nano-products: end-of-life assessment", *Journal of Nanoparticle Research*, Vol. 14, pp. 720.

Auffan, M. et al. (2010a), "Inorganic Manufactured Nanoparticles: How Their Physicochemical Properties Influence Their Biological Effects in Aqueous Environments", *Nanomedicine*, Vol. 5, No. 6, pp. 999-1007.

Auffan, M. et al. (2010b), "Structural Degradation at the Surface of a TiO_2-Based Nanomaterial Used in Cosmetics", *Environmental Science & Technology*, Vol. 44, No. 7, pp. 2689-2694.

Australia, Department of Health (2013), "Nano Silver Technical Information Sheet", National Industrial Chemicals Notification and Assessment Scheme (NICNAS), *www.nicnas.gov.au/communications/issues/nanomaterials-nanotechnology/nicnas-technical-activities-in-nanomaterials/nano-silver-health-hazard-review/nano-silver-technical-information-sheet* (accessed 2 April 2015).

Barton, L.E. et al. (2013), "Transformation of pristine and citrate-functionalized CeO_2 nanoparticles in a laboratory-Scale activated sludge reactor", *Environmental Science and Technology*, Vol. 48, No. 13, pp. 7289-7296.

Boeni, L. (2013), "Accumulation of Recovered Gold from Bottom Ash", Matriculation Paper, Hinwil (CH), *www.zar-ch.ch/en/home/news/news-en/datum/2013/01/29/maturitaetsarbeit.html*.

Boldrin, A. et al. (2014), "Environmental exposure assessment framework for nanoparticles in solid waste", *Journal of Nanoparticle Research*, Vol. 16, No. 6, pp. 2394.

Bolyard, S. et al. (2012), "The Fate and Transport of Nanoparticles in Municipal Solid Waste Landfills", University of Central Florida, *http://pure.ltu.se/portal/files/36938608/TR.Anders_Lagerkvist.Komplett.pdf*.

Bottero, J.Y. et al. (2015), "Nanotechnology, Global Development in the frame of Risk Forecasting, A necessity of interdisciplinary researches", *Comptes Rendus Géoscience*, Vol. 347, No. 1, pp. 35-42.

Brar, S.K. et al. (2010), "Engineered Nanoparticles in Wastewater and Wastewater Sludge", *Waste Management*, Vol. 30, pp. 504-520.

Breggin, L.K. and J. Pendergrass (2007), *Where Does the Nano Go? End-of-Life Regulation of Nanotechnologies*, Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies, PEN 10.

BSI (2007), *Nanotechnologies-Part 2: Guide to safe handling and disposal of manufactured nanomaterials*, British Standards, PD 6699-2:2007.

Bystrzejewska-Piotrowska, G. et al. (2009), "Nanoparticles: Their potential toxicity, waste and environmental management", *Waste Management*, Vol. 29, No. 9. pp. 2587-2595.

Chaudhry, Q. et al. (2009), *Nanolifecycle: A lifecycle assessment study of the route and extent of human exposure via inhalation for commercially available products and applications containing carbon nanotubes*, Food and Environment Research Agency, York, United Kingdom.

Cheng, X. et al. (2004), "Naphthalene adsorption and desorption from aqueous C-60 fullerene", *Journal of Chemical Engineering and Data*, Vol. 2004, No. 49, pp. 675-83.

DiSalvo, R. et al. (2008), *Evaluating the Impact of Nanoparticles on Wastewater Collection and Treatment Systems in Virginia*, Draper Aden Associates Inc.

EU (2015), "Nanomaterials: Case by Case Safety Approach for Breakthrough Technology", European Commission, *http://europa.eu/rapid/press-release_IP-12-1050_en.htm*.

EU (2012), "Types and uses of nanomaterials, including safety aspects", *Commission Staff Working Paper,* European Commission, *http://ec.europa.eu/health/nanotechnology/docs/swd_2012_288_en.pdf*.

EU (2008), "Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on Waste", *Official Journal of the European Union*, *http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:en:PDF*.

Farré, M. et al. (2009), "Ecotoxicity and analysis of nanomaterials in the aquatic environment", *Analytical and Bioanalytical Chemistry*, Vol. 393, No. 1, pp. 81-95".

Ganesh, R. et al. (2011), "Evaluation of Nanocopper Removal and Toxicity in Municipal Wastewaters", *Environmental Science and Technology*, Vol. 44, No. 20, pp. 7808-7813.

Ganzleben, C. et al. (2011), "Review of Environmental Legislation for the Regulatory Control of Nanomaterials", Milieu Ltd. and AMEC Environment & Infrastructure UK Ltd., *http://ec.europa.eu/environment/chemicals/nanotech/pdf/review_legislation.pdf*.

Gao, J. et al. (2008), "Nanowastes and the Environment: Using Mercury as an Example Pollutant to Assess the Environmental Fate of Chemicals Adsorbed onto Manufactured Nanomaterials", *Environmental Toxicology and Chemistry*, Vol.27, No. 4, pp. 808-810.

Gomez-Rivera, F. et al. (2012), "Fate of Cerium Dioxide (CeO2) Nanoparticles in Municipal Wastewater during Activated Sludge Treatment", *Bioresource Technology*, Vol. 108, pp. 300-304.

Gottschalk, F and B. Nowack (2011), "The release of engineered nanomaterials to the environment", *Journal of Environmental Monitoring*, Vol. 13, No. 5, pp. 1145-1155.

He, F. et al. (2012), "Rapid Removal of Hg(II) from Aqueous Solutions Using Thiol-Functionalized Zn-Doped Biomagnetite Particles", *ACS Applied Materials and Interfaces*, Vol. 4, pp. 4373-4379.

Health Council of the Netherlands (2011), *Nanomaterials in Waste*, The Hague: Health Council of the Netherlands, publication no. 2011/14E, *www.gezondheidsraad.nl/sites/default/files/Nano_waste_201114E.pdf*.

Holden, P. et al. (2014), "Five reasons to use bacteria when assessing manufactured nanomaterial environmental hazards and fates", *Current Opinion in Biotechnology*, Vol. 27, pp. 73-78.

Hyung, H. and J. H. Kim (2008), "Natural organic matter (NOM) adsorption to multiwalled carbon nanotubes: Effect of NOM characteristics and water quality parameters", *Environmental Science and Technology*, Vol. 42, No. 12, pp. 4416-4421.

Japan, Ministry of Environment (2009), *Guidelines for preventing the environmental impact of manufactured nanomaterials* (abstract, tentative translation June 2009), Expert committee on the environmental impact of manufactured nanomaterials, Ministry of the Environment, Japan.

Kaegi, R. et al. (2011), "Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant", *Environmental Science and Technology*, Vol. 45, No. 9, pp. 3902-3908.

Keller, A. A. et al. (2013), "Global life cycle releases of engineered nanomaterials", *Journal of Nanoparticle Research*, Vol. 15 No. 6.

Kim, B. et al. (2010), "Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products", *Environmental Science & Technology*, Vol. 44, No. 19, pp. 7509-7514.

Kiser, M. A. et al. (2009), "Titanium Nanomaterial Removal and Release from Wastewater Treatment Plants", *Environmental Science and Technology*, Vol. 43, No. 17, pp. 6757-6763.

Kiser, M. A. et al. (2010), "Biosorption of Nanoparticles to Heterotrophic Wastewater Biomass," *Water Research*, Vol. 44, No. 14, pp. 4105-4114.

Klaine, S. J. et al. (2008), "Nanomaterials in the environment: behaviour, fate, bioavailability, and effects", *Environmental Toxicology and Chemistry*, Vol. 27, No. 9, pp. 1825-51.

Lin, D. and B. Xing (2008), "Tannic acid adsorption and its role for stabilising carbon nanotube suspensions", *Environmental Science and Technology*, Vol. 42, No. 16, pp. 5917-5923.

Lozano, P. and N. D. Berge (2012), "Single-walled carbon nanotube behaviour in representative mature leachate", *Waste Management*, Vol. 32, No. 9, pp. 1699-1711.

Lui, Y. et al. (2014), "Nanoparticles in wastewaters: Hazards, fate and remediation", *Powder Technology*, Vol. 255, pp. 149-156.

Mueller, N.C. et al. (2012), "Nanomaterials in waste incineration and landfill", Internal Empa-report, *www.empa.ch/plugin/template/empa/*/124595*.

Mueller, N.C. et al. (2013), "Modelling the Flows of Engineered NMs during Waste Handling", *Environmental Science, Processes & Impacts*, Vol. 15, pp. 251-259.

Musee, N. (2011), "Nanowastes and the Environment: Potential New Waste Management Paradigm", *Environment International*, Vol. 37, No. 1, pp. 112-128.

NEEPH (2011), *Guidelines for Responsible Management of Waste Nanomaterials*, EKOTEK, EU FP7.

Nguyen, M.D. (2013), *Effects of CeO2 and ZnO nanoparticles on Anaerobic Digestion and Toxicity of Digested Sludge*, Dissertation, University of Dalat, Viet Nam.

Nowack, B. et al. (2013), "Potential release scenarios for carbon nanotubes used in composites", *Environment International*, Vol. 59, pp. 1-11.

OECD (2013), "Recommendation of the Council on the Safety Testing and Assessment of Manufactured Nanomaterials", *http://acts.oecd.org/Instruments/ShowInstrumentView.aspx?InstrumentID=298&InstrumentPID=314&Lang=en&Book=False*.

OECD (2004/2007), "Recommendation of the Council on the Environmentally Sound Management of Waste", C(2004)100, amended on 16 October 2007 – C(2007)97, OECD Paris, http://acts.oecd.org/Instruments/ShowInstrumentView.aspx?InstrumentID=51&InstrumentPID=48&Lang=en&Book=False.

PEN (2013), "The Project on Emerging Nanotechnologies, Consumer Products Inventory", PEN-Website, Washington DC, *www.nanotechproject.org/inventories/consumer/analysis_draft/* (accessed 2 April 2015).

Powell, M.C. et al. (2008), "Bottom-up risk regulation? How nanotechnology risk knowledge gaps challenge federal and state environmental agencies", *Environmental Management*, Vol. 42, No. 3, pp. 426-443.

Reinhart, D.R. et al. (2010), "Emerging contaminants: nanomaterial fate in landfills", *Waste Management*, Vol. 30, No. 11, pp. 2020-21.

Roes, L. et al. (2012), "Preliminary Evaluation of Risks Related to Waste Incineration of Polymer Nanocomposites", *Science of the Total Environment*, Vol. 417-418, pp. 76-86.

RCEP (2008), *Novel Materials in the Environment: The Case of Nanotechnology*, Royal Commission on Environmental Pollution.

Saleh, N.B. et al. (2010), "Influence of biomacromolecules and humic acid on the aggregation kinetics of single-walled carbon nanotubes", *Environmental Science and Technology*, Vol. 44, No. 7, pp. 2412-2418.

SCENIHR (2009), "Risk Assessment of Products of Nanotechnologies", Scientific Committee on Emerging and Newly Identified Health Risks, European Commission, DG Health & Consumers, Brussels, *http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_023.pdf*.

Siddique, S.N. (2013), "Simulation of Fate of Nanoparticles in Landfill Barrier Systems", Dissertation-University of Western Ontario (Canada).

SRU (2011), "Precautionary Strategies for Managing Nanomaterials (Vorsorgestrategien für Nanomaterialien, Sondergutachten)", German Advisory Council on the Environment (Sachverständigenrat für Umweltfragen), Berlin, *www.umweltrat.de/EN/TheGermanAdvisoryCouncilOnTheEnvironment/thegermanadvisorycouncilontheenvironment_node.html*.

Struwe, J. et al. (2012), "Bedeutung von Nanomaterialien beim Recycling von Abfällen (Importance of nanomaterials in the recycling of waste)", *Hans Böckler Stiftung Arbeitspapier (Hans Böckler Foundation Working Paper)*, AP 270.

Templeton, R.C. et al. (2006), "Life-cycle effects of single-walled carbon nanotubes (SWNTs) on an estuarine meiobenthic copepod", *Environmental Science and Technology*, Vol. 40, No. 23, pp. 7387-7393.

Tiede, K. et al. (2010), “Application of Hydrodynamic Chromatography-ICP-MS to Investigate the Fate of Silver Nanoparticles in Activated Sludge”, *Journal of Analytical Atomic Spectrometry*, Vol. 25, No. 7, pp. 1149-1154.

von der Kammer, F. et al. (2014), “Spot the Difference: Engineered and Natural Nanoparticles in the Environment-Release, Behavior, and Fate”, *Angewandte Chemie International Edition, Special Issue: Nanotechnology & Nanomaterials, Nanotoxicology & Nanomedicine*, Vol. 53, No. 46, pp. 12398-12419.

Walser, T. et al. (2012), “Persistence of Engineered Nanoparticles in a Municipal Solid Waste Incineration Plant”, *Nature Nanotechnology*, Vol. 7, pp. 520-524.

Wang, Y. et al. (2012), “Fate and Biological Effects of Silver, Titanium Dioxide, and C60 (Fullerene) Nanomaterials during Simulated Wastewater Treatment Processes”, *Journal of Hazardous Materials*, Vol. 201-202, pp. 16-22.

Westerhoff, P. et al. (2013), “Nanomaterial Removal and Transformation during Biological Wastewater Treatment”, *Environmental Engineering Science*, Vol. 30, No. 3, pp. 109-120.

WWICS (2011), “Nanotechnology Consumer Products Inventory”, Woodrow Wilson International Center for Scholars, Project on Emerging Technologies, *www.nanotechproject.org/inventories/consumer/* (accessed 8 April 2015).

Yang, Y. et al. (2013), “Nanosilver impact on methanogenesis and biogas production from municipal solid waste”, *Waste Management*, Vol. 32, pp. 816-825.

Yang, Y. et al. (2006), “Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials”, *Environmental Science and Technology,* Vol. 40, No. 6, pp.1855-1861.

Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 2

Recycling of waste containing nanomaterials

This chapter reviews the current state of knowledge on the fate of nanomaterials in recycling operations and identifies the areas where further work on the environmentally sound management of waste containing nanomaterials would be needed. It explores the risks related to nanomaterials in waste, the effectiveness of best available techniques (BAT) and the consequences of non-standard treatment of waste. The chapter also identifies key knowledge gaps and possible areas for further research.

Today, the number of new commercial products containing nanomaterials is growing (PEN, 2013). Many such products are in the personal care/cosmetics/sunscreen categories. The unused leftovers and their packaging, as well as other products containing nanomaterials – such as electronic equipment, textiles or composite plastics – end their life cycle as municipal or industrial waste. They are treated by recycling, energy recovery, waste incineration or landfill, as defined in the hierarchy of waste management options. Recycling in general has a higher priority than incineration and/or landfill (EU, 2008), (OECD, 2004/2007).

Today, products containing nanomaterials are being recycled along with their analogous products without nanomaterials. No separation or separate collection of product containing nanomaterials solely due to their nanomaterial-content is known. Also, the existing recycling techniques do not take into account the possible nanospecific risks coming from waste containing nanomaterials.

Recycling operations are not always carried out with techniques that meet the standards of an environmentally sound waste management, with the associated risks for health, safety and environment, even with products that do not (or not yet) contain nanomaterials. If operations are not managed to environmentally sound waste management standards, this may give raise to a lot of potential other problems.

The main objective of this report is to review the current state of knowledge on the fate of nanomaterials in the course of recycling operations and identify the areas where further work on the environmentally sound management of waste containing nanomaterials (WCMN) would be needed.

The chapter first explains the importance of recycling in waste management and identifies key nanomaterials. It then investigates the fate of nanomaterials, explores the risks related to nanomaterials in waste and covers best available techniques (BAT) and issues of non-standard treatment of waste. The chapter concludes by identifying key knowledge gaps and possible areas for further research.

The importance of recycling in waste management

Recycling of waste is one element in strategies of waste minimisation or waste prevention (OECD, 2000) and of sustainable materials management SMM (OECD, 2012). Individual countries and international bodies are setting recycling goals and are taking measures to reach them. In the EU, several legal provisions exist with obligation for the member states (EU, 2008), (EEA, 2013) to recycle municipal waste and/or household waste. In the United States, the Environmental Protection Agency (US EPA) regulates household, industrial, manufacturing and commercial solid and hazardous wastes under the Resource Conservation and Recovery Act (RCRA). Effective solid waste management is a cooperative effort involving federal, state, regional, and local entities.

In the OECD, the average recycling rate (including composting) for municipal waste was estimated at 33% in 2011, with a range from less than 10 per cent to 63 per cent (OECD

Statistics[1]). In the EU, the overall rate of material recovery (recycling plus composting) amounts to 42%, the range in individual countries is given as going from 2% to 70% (Blumenthal, 2011).

Based on different sources, the main waste streams recycled in municipal and industrial waste are listed below [(Fischer and Davidsen, 2010), (US EPA, 2013), (FOEN, 2012), (OECD Statistics)]. In addition, there is a growing interest of the recycling industry to recover metals and mineral secondary raw materials from bottom ash ("slag") of Municipal Solid Waste Incinerators MSWI (Boeni, 2013). This waste stream is also included in the following list:

- ✓ Bio waste
- ✓ Food waste
- ✓ Glass (bottles)
- ✓ Metal
- ✓ Paper and cardboard
- ✓ Plastic (PET and various other plastics)
- ✓ Leather and textiles
- ✓ Waste electronic and electrical equipment (WEEE)
- ✓ Batteries
- ✓ Wood
- ✓ Construction and demolition wastes
- ✓ End of Life Vehicles (ELV)
- ✓ Tires
- ✓ Recycling of residues from waste incineration plants (recovery of metals from bottom ash by mechanical separation or from fly ash by acid washing)

Processes where nano-related waste streams can be generated include production, distribution, handling (and use) as well as waste treatment (NEEPH, 2011). It is anticipated that, as the production and number of nanomaterial applications increase, waste streams containing nanomaterials will also increase, and in addition to naturally occurring nanoparticles, engineered nanomaterials possibly might become more widespread in the environment, if insufficient knowledge about the fate and associated risks of nanomaterials released from waste treatment operations, as recycling, could result in inadequate management.

Key nanomaterials in products

When discussing the problem of recycling of WCNM, some product categories are particularly significant as potentially ENM-containing products and thus leading to WCNM. From different sources, nanomaterial containing products and nanomaterial types have been compiled in Struwe et al. (2012), PEN (2013) for consumer products, Lee et al. (2010) and Grebler and Gazso (2012) for construction material and NEEPH (2011) on the use of nanomaterials in composite plastics ("Nanocomposites").

Table 2.1 provides a list of nanomaterials which may be contained in consumer products, with specific examples.

Table 2.1. **Summary of reported nanomaterials in WCNM**

Nanomaterial	Consumer products (Struwe et al., 2012) (PEN, 2013) (NEEPH, 2011)	Construction material (Lee et al., 2010) (Grebler and Gazso, 2012)
Carbon Nanotubes CNT	Electronic devices, sports equipment, composite plastics	Concrete, ceramics
Fullerene	Semi-conductor technology	
nano-Silver (nAg)	Textiles, anti-bacterial kitchenware	Antibacterial coatings and paints
Carbon Black (CB)	Tires, printing toner, plastics	
nano Titanium dioxide ($nTiO_2$)	Paints, coatings, composite plastics	Self-cleaning coatings
nano Silicium dioxide (amorphous and crystalline ($nSiO_2$)*)*	Coatings, composite plastics, tires,	Concrete, ceramics, window coatings
nano Zinc oxide (nZnO)	cosmetics, coatings and paints,	
nano Titanium nitride (nTiN)	PET-bottles	
nano Iron oxides ($n\ FeO/Fe_2O_3$)	Electronic devices	Concrete
Nano Ceriumoxide ($nCeO_2$)	Fuel additive	Anti-corrosive coatings
Nano Phosphate ® ($nLiFePO_4$)	Li-Batteries	
Nano Copper particles (nCu)		improved steel (anticorrosive)

Fate of nanomaterials in recycling operations and potential exposure

Waste recycling has many facets: there is a wide variety of recyclable materials within a waste stream; there are various recycling methods, more or less technically adapted to the specific waste stream and/or secondary raw material to be recovered. The appendix to this report includes a table listing some waste streams with possible WCNM, a short description of recycling procedures, and known nanomaterials.

The main concern about possible nanospecific risks of WCNM in recycling processes are nano-objects that might be released into the workplace atmosphere, or into the environment by way of the air, water and or soil (Struwe et al., 2012; NEEPH, 2011; FOEN, 2010).

Information about the fate of nanomaterials in recycling processes is only beginning to emerge. Mostly, exposure scenarios are based on modelling, and not on evidence. It is extremely difficult to quantify and monitor the long-term release of ENM during the final disposal of ENM containing products. (Gottschalk & Nowack, 2011). A "Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterials in Workplace Operations" has been proposed by a group of several German institutes (Tiered Approach, 2011), which may give guidance in assessing also the release of ENMs during recycling operations.

Potential risks of exposure depend on the specific recycling processes to which the WCNM is subject. Shredding, milling and thermal processing may result in high exposure potentials, if not operated in enclosed processes. If filters are not designed for nanoparticles, there may be exhaust to the environment. Manual dismantling may cause release of nano-objects and direct exposure of workers (Koehler et al., 2008). A transfer of unwanted or even detrimental nanomaterials to recycled materials ("cross-contamination") may occur and may possibly be detrimental to the quality of the recycled materials (Chaudhry et al., 2009).

Risks related to nanomaterial in waste

During the recycling of Waste Containing Nanomaterials, engineered nanoparticles, like any other particle in the recycling process, might remain individually isolated or form new bigger agglomerates. Nanorelevant potential exposure exists mainly in connection with free nano-objects that are in the nanoscale (smaller than 100 nm) in all three or in two spatial dimensions (nanoparticles, nanofibers, nanorods) (British Standards, 2007):

- Nanoparticles may penetrate biological barriers.
- They may show intensified effects in the case of substances with toxic properties.
- They may have increased bioavailability.
- They may have different chemical and physical properties from the "parent" material.
- Some types of CNT (carbon nanotubes) and nanowires may have similar effects in the lungs to asbestos fibres.
- Attention must be paid to the risk of dust explosions (as in all applications of inflammable powders or powdery substances).

These possible exposures must be taken into account when managing waste containing nanomaterials, especially nano-objects that are free or that are releasable (e.g. due to the recycling process). Guidance for the safe recovery and disposal of waste containing nanomaterials has been given for example in VCI (2012).

Much research has been done and is still done on health, safety and environment impacts of nanomaterials and on their toxicology and ecotoxicology (JRC/ESAC 2011, Mikkelsen et al., 2011). *"Health and environmental hazards have been demonstrated for a variety of manufactured nanomaterials"*, however "*Not all nanomaterials induce toxic effects. Some manufactured nanomaterials have already been in use for a long time* (e.g. *carbon black,* TiO_2) *showing low toxicity. Therefore, the hypothesis that smaller means more reactive, and thus more toxic, cannot be substantiated by the published data. In this respect, nanomaterials are similar to normal chemicals/substances in that some may be toxic and some may not. As there is not yet a generally applicable paradigm for nanomaterial hazard identification, a case-by-case approach for the risk assessment of nanomaterials is still recommended*" (SCENIHR, 2009).

The wide variety of consumer products makes it difficult to devise and verify a generic exposure assessment and risk management for nanoproducts as a class (JRC/ESAC, 2011). Publications which address the risk-potential associated with consumer products when they enter the recycling process are found in (Struwe et al., 2012; Ostertag & Huesing, 2007; Kuhlbusch & Nickel, 2010). Examples of studies on specific nanomaterials are (Burkhardt et al., 2011) on Silver, (Nanosustain[2]) on ZnO and Nanocellulose, (Mikkelsen et al., 2011) on Titanium dioxide; Cerium dioxide; Fullerenes (Carbon balls); Silver; Zero-valent iron; Silicium dioxide and Nanoclay.

There is still uncertainty about the effective nano-specific risks of ENM in recycled waste streams containing nanomaterials, because there exist no or only a few studies. In the best case, the data are just sufficient to make a preliminary assessment (Struwe et al., 2012). Examples are risks coming from carbon nanotubes which, due to their specific form, may show cancerogenic effects in the lung. Nanosilver is used in textiles and other products because of its biocide (antibacterial) properties, which may bring a risk potential if free nanosilver reaches the environment.

The potential risk of a specific ENM in a waste stream is not only a function of the toxicity or ecotoxicity of the nanomaterial. Additional factors may determine the risk potential of a nanomaterial during recycling, and further research is needed to clarify these issues:

- Quantity / concentration of the ENM in the product or in the waste stream.
- The mode of incorporation of ENM in the product: Are they in a free form, associated with other materials, or fixed by chemical binding?
- Will the ENM be set free with a specific recycling operation?
- Will free ENM stay as single nanoparticles or nanorods or will they agglomerate to bigger entities?
- Will secondary materials (e.g. plastics or construction materials) produced from recycling processes be contaminated in an uncontrolled manner by the ENM enclosed in the original products containing nanomaterials (cross-contamination) which have been recycled?

However, there is enough uncertainty and suspicion of harm to invoke preventive measures (FOEN, 2010; Japan Ministry of Environment, 2009; BSI, 2007; Luther et al., 2004) against the potential nanospecific risks for health or environment during recycling of waste containing nanomaterial.

Recycling procedures and Best Available Techniques (BAT)

Recycling operations shall be done in an environmentally sound manner, according to the Best Available Techniques and by the Best Environmental Practices (BAT/BEP) (OECD, 2004/2007; OECD, 2007); (EU, 2008). The EU proposes *the integration of assessment of risk to human health, the environment, consumers and workers at all stages of the life cycle of the technology (including conception, R&D, manufacturing, distribution, use and disposal) (EU, 2004)*. In view of the uncertainties concerning the fate of nanomaterials during recycling processes, this may also be useful as a precautionary measure to mitigate possible exposure to ENM.

During recycling operations, the main possibilities of exposure to nanomaterials in the recycling process of waste streams that may contain WCNM may be (Struwe et al., 2012):

- Exposure to fine or ultrafine dust containing free nano-objects emitted during transport, sorting, shredding, grinding or pouring of the WCNM.
- Exposure to nano-objects in liquid media (water, solvents) due to cleaning or rinsing the products before mechanical recycling; also exposure to contact with nano-objects on cleaning clothes from maintenance and cleaning of recycling equipment.
- Exposure to nano-objects that may be set free in the flue gas or to the ambient air with thermal processes (heating, welding, pyrolysis) when there is insufficient occupational control.

If by an assessment of possible risks it is known or suspected that nanoparticles are released during production, handling or further processing, workers' exposure to ENMs can be prevented by taking the following safety measures by this order of priority (Luther et al., 2004; BSI, 2007; Japan Ministry of Environment, 2009; FOEN, 2010; VCI/BAuA, 2012; BAuA, 2013):

1. Technical measures at the source, e.g. use of hermetically sealed apparatus; minimisation of dusts and aerosols; extraction of dusts and aerosols directly at the source; filtering of extracted air, if necessary isolation of the workroom and appropriate

modification of room ventilation; cleaning of recycling equipment by vacuum cleaning with suitable appliances or wiping with a damp cloth, but not by blowing off;

2. Organisational measures, e.g. minimisation of the exposure time; minimisation of the number of persons exposed; restriction of access; instructions of personnel concerning hazards and protection measures;
3. Personal protective measures: respiratory protection with particle filters P3; protection gloves; closed goggles; protection suit (non-woven).

Recommendations and guidelines on safe management of engineered nanomaterials have been published by several public and private organisations (e.g. Luther et al., 2004; BSI, 2007; FOEN, 2010; Japan Ministry of Environment, 2009; NEEPH, 2011), and the OECD recommendation *C(2004)100* on Environmentally Sound Management of waste (OECD, 2004/2007) includes exposure prevention measures.

The issue of non-standard treatment of waste

Struwe et al. (2012) distinguish between two categories of recycled WCNM:

a) WCNM with heterogeneous composition, containing different products in their waste stream. Additionally, the different products also contain multiple diverse nanomaterials, often not even known. This category includes for example WEEE, end-of-life vehicles, paper and most plastic waste.

b) WCNM with comparatively homogeneous composition, containing only few, normally known nanomaterials, e.g. PET-bottles, used tires, Li-ion batteries.

It seems reasonable to assume that emission control with WCNM of the first category will pose more difficulties, because of the diversity of products and nanomaterials and/or the complexity of the recycling technique (e.g. with WEEE, ELV or CDW).

We can suppose that the application of known techniques for workers and environment protection would also in a general way decrease the risk, when there are nanomaterials in the waste stream (Japan Ministry of Environment, 2009; FOEN, 2010; NEEPH, 2011; SRU, 2011; Struwe et al., 2012; Boeni, 2013).

By applying appropriate BAT procedures for waste treatment[3], emissions in general will be lowered, and it can be expected that possible exposure to ENM will also be lowered. The following list gives a short selection of elements mentioned in the cited document that may be considered as BAT when handling waste:

- Environment Management System in order to know the processes, the accepted waste and the waste and secondary products going out of the treatment installation;
- Ensure proper location and drainage of storage facilities;
- Unloading solids and sludge in closed areas;
- Perform crushing/shredding and sieving operations in areas fitted with extractive vent systems linked to abatement equipment when handling materials that can generate emission to air (e.g. odours, dust, VOCs);
- Proper management of waste water from the treatment plant;
- Air emission treatment;
- Management of process residues;
- Avoid soil contamination.

The following statement made by the British Health and Safety Executive about BAT/BEP to apply with WEEE-Recycling does not refer to WCNM, but to substances like mercury or lead. However, The principle formulated here may – "mutatis mutandis" – give good guidance when implementing BAT in recycling technologies where there is to expect WCNM in the waste stream:

> *"As a result of this complex mix of product types and materials, some of which are hazardous (including arsenic, cadmium, lead and mercury and certain flame retardants) WEEE recycling poses a number of health risks that need to be adequately managed. For example, exposure to substances released during processing (such as mercury released from fluorescent tubes, lead and phosphorous pentachloride as a result of breaking cathode ray tubes). It is important to stress that if effective measures are taken to control exposure to mercury and lead, then normally the control of exposure to other hazardous substances should also be adequate".*[4]

This adequacy is true when releases and exposures to the nanomaterials may occur in the same recycling process steps that are specifically controlled to reduce or eliminate releases and exposures to mercury and lead.

Knowledge gaps and possible activities

The principal challenges with safe and environmentally sound recycling procedures for waste containing nanomaterials are:

a) controlling the health, safety and environmental risks arising from recycling processes of waste containing nanomaterials;

b) controlling the technical and environmental quality of secondary materials that may be contaminated with ENM from the original waste stream;

c) developing technologies that may be used for the recovery of the ENM from the products, given suitable quantities, concentrations and economic value of the ENMs.

Several authors who have identified knowledge gaps in the context of recycling of WCNM recommend actions that can be taken in order to improve the current uncertainty (Japan Ministry of Environment, 2009; Struwe et al., 2012; NEEPH, 2011; Gottschalk & Nowack, 2011; Kuhlbusch & Nickel, 2010; FOEN, 2010; Lee et al., 2010). From these statements, the most important knowledge gaps and proposed measures in the context of recycling of WCNM can be summarised in Table 2.2 as follows:

Table 2.2. **Knowledge gaps and proposed measures in the context of recycling of WCNM**

Knowledge gaps and open questions	Possible activities
Types and quantities of nanomaterials in products and waste and associated risk potentials?	● Evaluation of types and quantities of specific nano-materials in waste streams ● Labelling of products containing nanomaterials ● Produce experimental and analytical data about the main release sources during all ENM life stages: ENM production, manufacturing of nanoproducts, consumption and disposal of nanoproducts.
Behaviour and fate of the nanomaterials in products during the recycling processes (from collection to the preparation of the recycled products): do they stay in the material, are they set free and if so, are they in a form that is a risk for health, safety and environment HSE)?	● Research on the risk of release of NPR from composite products during waste treatment (e.g. with shredding) ● Produce experimental and analytical data regarding the form the ENM are released, such as whether the ENM are agglomerated or present as single particles or if they are embedded within a matrix ● Additional research on the possibilities that nanomaterials from WCNM "diluted" to other materials during the recycling procedure may impair the quality of these materials
The most suitable technologies for emission control and for protection of humans and the environment when recycling WCNM?	● Identification of possible sources of ENM emissions and of the concerned workplaces in the recycling industry ● Preventive measures on the basis of existing guidelines and knowledge for health protection and workplace safety ● Research on the effectiveness of the current waste management systems' suitability of dealing with new pollutants containing nanoscaled structures ● Implementation of preventive measures on the basis of existing guidelines and knowledge for health protection and workplace safety ● Development of dedicated guidelines for the recycling industry
Measurement and identification of ENM in products and waste streams	● Development of methods and standardisation of "emission measurements" with examination of the relevant parameters with respect to norms.
Effects of cross-contamination of recycled materials with nanomaterials from WCNM	● Additional research on the possibilities that nanomaterials from WCNM may be "diluted" to other, downcycled materials during the recycling procedure ● Research on how far nanomaterials can interfere with or prevent recycling and other recovery processes
Possibility of recovery of nanomaterials from a waste stream	● Evaluation of eventual need for separate collection for specific types of waste containing nanomaterials, for example because of the quantities expected or because they are hazardous.

Notes

1. OECD Statistics *http://stats.oecd.org/Index.aspx?DataSetCode=WASTE*.
2. *www.nanosustain.eu/component/content/article/1-latest-news/128-nanosustain-factsheet-and-case-studies*.
3. For guidance on the implementation of BAT in the waste sector, see EU/IPPC-Document on Best Available Techniques for the Waste Treatment Industries (EU-IPPC, 2006, *http://eippcb.jrc.ec.europa.eu/reference/*), even if it is not mentioning Waste Containing Nanomaterial at all.
4. UK Health and Safety Executive *www.hse.gov.uk/waste/waste-electrical.htm*.

References

BAuA (2013), "Announcement on Hazardous Substances, Manufactured Nanomaterials", German Federal Institute for Occupational Safety and Health (BAuA), Committee on Hazardous Substances (AGS), Announcement 527, No. 25, pp. 498-511, Berlin, *www.baua.de/en/Topics-from-A-to-Z/Hazardous-Substances/TRGS/Announcement-527.html*.

Mudgal, S. et al. (2011), *Study on Coherence of Waste Legislation,* Final Report prepared for the European Commission (DG ENV), BIO Intelligence Service, Paris.

Blumenthal, K. (2011), "Generation and Treatment of Municipal Waste", Statistics in Focus, EUROSTAT, 31/2011, Luxembourg, *http://ec.europa.eu/eurostat/documents/3433488/5579064/KS-SF-11-031-EN.PDF/00c0b3fe-db08-4076-b39a-e92015ce99e0*.

Boeni, L. (2013), "Accumulation of Recovered Gold from Bottom Ash", Matriculation Paper, Hinwil (CH), *http://zar-ch.ch/fileadmin/user_upload/Contentdokumente/Oeffentliche_Dokumente/2013_Maturitaetsarbeit_L_Boeni.pdf*.

Burkhardt, M. et al. (2011), “Entsorgung nanosilberhaltiger Abfälle in der Textilindustrie – Massenflüsse und Behandlungsverfahren (Disposal nanosilver containing waste in the textile industry – Mass flows and methods of treatment)”, HSR Hochschule für Technik Rapperswil, Institut für Umwelt und Verfahrenstechnik (UMTEC), Rapperswil (CH), *www.umtec.ch/uploads/tx_hsrpm/120310_Studie_NanAgTex_Abschlussbericht_BAFU_Final_01.pdf*.

Chaudhry, Q. et al. (2009), “Nanolifecycle: A lifecycle assessment study of the route and extent of human exposure via inhalation for commercially available products and applications containing carbon nanotubes”, Food and Environment Research Agency, York, United Kingdom, *http://randd.defra.gov.uk/Document.aspx?Document=CB0423_9128_FRP.pdf*.

DEFRA (2006), *Guidance on Best Available Treatment Recovery and Recycling Techniques (BATRRT) and treatment of Waste Electrical and Electronic Equipment (WEEE)*, Department for Environment, Food and Rural Affairs, London, *http://webarchive.nationalarchives.gov.uk/20130402151656/http://archive.defra.gov.uk/environment/waste/producer/electrical/documents/weee-batrrt-guidance.pdf*.

Fischer, C. and C. Davidsen (2010), “Europe as a Recycling Society: The European Recycling Map”, *ETC/SCP Working Paper No 5, 2010*, EIONET, European Topic Centre on Sustainable Consumption and Production, Copenhagen, *http://scp.eionet.europa.eu/publications/WP2010_5_The%20European%20Recycling%20Map*.

Fischer, C. and M. Werge (2009), “Europe as a Recycling Society: Present recycling levels of Municipal Waste and Construction & Demolition Waste in the EU”, *ETC/SCP working paper No. 2, 2009*, EIONET, European Topic Centre on Sustainable Consumption and Production, Copenhagen, *http://scp.eionet.europa.eu/publications/wp2009_2*.

Fischer, C. et al. (2013), “Managing municipal solid waste – a review of achievements in 32 European countries”, *European Environment Agency Report No2, 2013*, Copenhagen, *www.eea.europa.eu/publications/managing-municipal-solid-waste*.

EU (2008), “Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on Waste”, *Official Journal of the European Union*, *http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:312:0003:0030:en:PDF*.

EU (2004), *Towards a European strategy for nanotechnology*, European Commission, Brussels, *https://ec.europa.eu/research/industrial_technologies/pdf/policy/nano_com_en_new.pdf*.

EU/IPPC (2006), “Integrated Pollution Prevention and Control: Reference Document on Best Available Techniques for the Waste Treatment Industries”, IPPC Bureau, Seville, *http://eippcb.jrc.ec.europa.eu/reference/*.

Fierz, R. and R. Bunge (2007), “Trockenaustrag von KVA-Schlacke (Dry Discharge of Bottom Ash)”, Summary of the project, FOEN, Bern, *www.bafu.admin.ch/abfall/01495/01496/index.html?lang=de&download=NHzLpZeg7t,lnp6I0NTU042l2Z6ln1acy4Zn4Z2qZpnO2Yuq2Z6gpJCFdIF3gGym162epYbg2c_JjK*.

FOEN (2012), *Swiss Federal Office for the Environment, Multi Year Waste Statistics, Factsheets*, Bern.

FOEN (2010), *Environmentally sound and safe disposal of waste from manufacturing and industrial and commercial processing of synthetic nanomaterials*, Swiss Federal Office for the Environment (FOEN), Bern.

Gottschalk, F and B. Nowack (2011), “The release of engineered nanomaterials to the environment”, *Journal of Environmental Monitoring*, Vol. 13, No. 5, pp. 1145-1155, Cambridge, United Kingdom.

Grebler, S. and A. Gazso (2012), “Nano in the Construction Industry”, Nano Trust Dossiers- Institute of Technology Assessment of the Austrian Academy of Science, Vol. 2012, No. 32, pp. 1-6, Vienna.

Hendren et al. (2011), “Estimating Production Data for Five Engineered Nanomaterials As a Basis for Exposure Assessment”, *Environmental Science & Technology*, Vol. 45, No. 7, pp. 2562-2569, ACS Publication.

Honnert, B. and R. Vincent (2007), “Production et utilisation industrielle des particules nanostructurées (Production and industrial use of nanostructured particles)”, Hygiène et sécurité du travail – Cahiers de notes documentaires – 4e trimestre 2007 (Health and safety at work – Papers briefing notes – 4th Quarter 2007, Institut National de Recherche et de Sécurité (INRS), Département Métrologie des Polluants, (National Research and Safety Institute, Pollutant Metrology Department), Paris, *www.inrs.fr/accueil/produits/mediatheque/doc/publications.html?refINRS=ND%202277*.

Japan, Ministry of Environment (2009), *Guidelines for preventing the environmental impact of manufactured nanomaterials* (abstract, tentative translation June 2009), Expert committee on the environmental impact of manufactured nanomaterials, Ministry of the Environment, Japan.

JRC/ESAC (2011), *Impact of Engineered Nanomaterials on Health: Considerations for Benefit-Risk Assessment*, EASAC Policy Report – JRC Reference Report, European Commission Joint Research Centre Institute for Health and Consumer Protection (IHCP), Ispra (I), *http://publications.jrc.ec.europa.eu/repository/handle/JRC64792*.

Koehler, A. et al. (2008), "CNT in Li-Ion-Batteries and Synthetic Textiles: Studying the potential release of carbon nanotubes throughout the application life cycle", *Journal of Cleaner Production*, Vol. 16, No. 8-9, pp. 927-937.

Kulbusch, T. and C. Nickel (2010), *Emission von Nanopartikeln aus augewählten Produkten im Lebenszyklus (Emission of nanoparticles from selected products during their life cycle),* Institut für Energie und Umwelttechnik (IUTA) e.V.,Bereich „Luftreinhaltung & Nachhaltige Nanotechnologie (Institute for Energy and Environmental Technology (IUTA) eV, The "Air Quality & Sustainable Nanotechnology") (funded by German Umweltbundesamt UBA), On behalf of the Federal Environment Agency (Germany), Duisburg.

Lee, J. et al. (2010), "Nanomaterials in the Construction Industry: A Review of Their Applications and Environmental Health and Safety Considerations", *ACS Nano*, Vol. 4, No. 7, pp. 3580-3590, Washington DC.

Luther, W. et al. (2004), "Industrial application of nanomaterials – chances and risks", VDI Technologiezentrum, Dusseldorf, *www.vditz.de/publikation/industrial-application-of-nanomaterials-chances-and-risks/*.

Mikkelsen, S.H. et al. (2011), "Survey on basic knowledge about exposure and potential environmental and health risks for selected nanomaterials", *Environmental Project No. 1370*, Danish Environment Protection Agency, Copenhagen, *www2.mst.dk/udgiv/publications/2011/08/978-87-92779-09-0.pdf*.

NEEPH (2011), *Guidelines for Responsible Management of Waste Nanomaterials*, EKOTEK, EU FP7.

OECD (2014), "OECD Waste Statistics", *OECD Environment Statistics*, http://stats.oecd.org//Index.aspx?QueryId=69014.

OECD (2012), *Sustainable Materials Management: Making Better Use of Resources*, OECD Publishing; Paris, *http://dx.doi.org/10.1787/9789264174269-en*.

OECD (2007), *Guidance Manual on Environmentally Sound Management of Waste*, OECD, Paris, *http://dx.doi.org/10.1787/9789264042049-en*.

OECD (2004/2007), "Recommendation of the Council on the Environmentally Sound Management of Waste", C(2004)100, amended on 16 October 2007 – C(2007)97, OECD Paris, *http://acts.oecd.org/Instruments/ShowInstrumentView.aspx?InstrumentID=51&InstrumentPID=48&Lang=en&Book=False*.

OECD (2000), "Strategic Waste Prevention", *OECD Reference Manual*, OECD, Paris, *www.oecd.org/officialdocuments/publicdisplaydocumentpdf/?doclanguage=en&cote=env/epoc/ppc(2000)5/final*.

Ostertag, K. und B. Huesing (2007), "Nanomaterialien in der Abfallwirtschaft. Identifizierung prioritärer Ansatzpunkte für eine Expositionsbewertung am Beispiel von Altfahrzeugen und Altpapier (Nanomaterials in waste management. Identification of starting points for an exposure assessment using the example of car wrecks and waste paper)", in Bilitewski, B.; Schnurer, H.; Zeschmar-Lahl, B. (eds.), *Müllhandbuch, 2. Aufl. (Waste Manual, 2nd ed.)*, 8054.1-8054.27, Erich Schmidt, Berlin.

PEN (2013), "The Project on Emerging Nanotechnologies, Consumer Products Inventory", PEN-Website, Washington DC, *www.nanotechproject.org/inventories/consumer/analysis_draft/* (accessed 2 April 2015).

Peters, F. (2012), "End-of-life tyres including nanomaterials", Presentation OECD WPRPW Munich Workshop, May 2012.

Piccinno, F. et al. (2012), "Industrial Production Quantities and Uses of Ten Engineered NMs in Europe and the World", *Journal of Nanoparticle Research*, Vol. 14, No. 9, pp. 1109- 1120.

SCENIHR (2009), "Risk Assessment of Products of Nanotechnologies", Scientific Committee on Emerging and Newly Identified Health Risks, European Commission, DG Health & Consumers, Brussels, *http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_023.pdf*.

Simkó, M. and R. Fries (2012) “(Nano)-Titanium dioxide (Part III): Environmental effects”, Nano Trust Dossiers- Institute of Technology Assessment of the Austrian Academy of Science, Vol. 2012, No. 35, pp. 1-3, Vienna.

SRU (2011), “Vorsorgestrategien für Nanomaterialien, Sondergutachten (Precautionary Strategies for Managing Nanomaterials)”, Sachverständigenrat für Umweltfragen (German Advisory Council on the Environment), Berlin, *www.umweltrat.de/EN/TheGermanAdvisoryCouncilOnTheEnvironment/thegermanadvisorycouncilontheenvironment_node.html*.

Struwe, J. et al. (2012), “Bedeutung von Nanomaterialien beim Recycling von Abfällen (Importance of nanomaterials in waste recycling)”, *Hans Böckler Stiftung Arbeitspapier (Hans Böckler Foundation Working Paper)*, AP 270, November.

Swiss Government (2008), “Swiss Government: Action Plan Synthetic Nanomaterials”, Bern, 2008, *www.bafu.admin.ch/publikationen/publikation/00574/index.html?lang=en*.

Tiered Approach (2011), “Tiered Approach to an Exposure Measurement and Assessment of Nanoscale Aerosols Released from Engineered Nanomaterials in Workplace Operations”, Air Quality and Sustainable Nanotechnology, Institute of Energy and Environmental Technology e. V. (IUTA); Federal Institute for Occupational Safety and Health (BAuA); German Social Accident Insurance Institution for the Raw Materials and Chemical Industry (BG RCI); German Chemical Industry Association (VCI), Institute for Occupational Safety and Health of the DGUV (IFA); Research Group Mechanical Process Engineering, Institute of Process Engineering and Environmental Technology, Technical University Dresden (TUD), August, Germany.

US EPA (2013), “Municipal Solid Waste in the United States: 2011 Facts and Figures”, Office of Solid Waste, United States Environmental Protection Agency, Washington DC, 2013, *www.epa.gov/osw/nonhaz/municipal/msw99.htm*.

VCI (2012), “Guidance for the Safe Recovery and Disposal of Wastes containing Nanomaterials”, Association of the German Chemical Industry (VCI), Frankfurt am Main.

VCI/BAuA (2012), “Guidance for Handling and Use of Nanomaterials at the Workplace”, Association of the German Chemical Industry (VCI)/ German Federal Institute for Occupational Safety and Health (BAuA), Frankfurt/Berlin.

ANNEX 2.A1

Waste streams possibly containing nanomaterials

Table 2.A1.1. **Selected waste streams with possible WCNM**

Waste type	Recycling procedure	Nanomaterials	Theoretically possible sources of nano object emissions in the recycling process
Metal waste (scrap)	Shredding, smelting	In coatings: Metal oxides, CNT, SiO_2	Shredding, if ENM can be set free from coatings Smelting: ENM that are not destroyed in the melting process, insufficient exhaust gas purification
Paper and cardboard	Pulping, de-inking (wet processes) *www.paperonline.org/environment/paper-recycling/the-paper-recycling-process*	Carbon Black (from the ink), TiO_2 (except for special papers, TiO2 is not in the nano-form)	Dust from collection, transport Aerosols of ink from pulping and de-inking
Plastic	Collect & sorting, or separate collection (e.g. for PET-bottles) mechanical recycling: shredding, washing, regranulation Feedstock recycling: depolymerisation, cracking (for basic chemicals)	CNT, SiO_2, TiO_2	Shredding and regranulation: if nano objects are set free. Feedstock (chemical) recycling: nano objects that are not destroyed in the process may be emitted or end up in the cracking residues (tar). Problem of dispersion of ENM to regranulated plastics
Textiles	Collect, reuse, sorting, preparing for reuse, shredding to get fibres	CNT, Ag	Shredding: if nano objects are set free
Waste Electronic and Electrical Equipment (WEEE)	Collect, dismantling, sorting by hand, shredding and separation of the fractions, processing of fractions (non-magnetic metals, iron, glass, plastics etc.), further processing of the components (metal melting, material recovery of iron and non-iron metals, extraction of metals from circuit boards	Carbon black (in plastic and in toners), CNT (in electronic devices and in plastic housings, nano-Iron oxide, ZnO, SiO_2, Ag (in coatings)	Any step of the procedure, depending on the nanomaterial containing component and on the specific type of nanomaterial.
Batteries	Collect, sorting. Mechanical/chemical and/or thermal treatment (various procedures, e.g. BATREC (Switzerland)[1] for alkali- and mercury batteries, Battery Solutions (USA)[2], Toxco (USA)[3] for lithium batteries, or INMETCO (USA) for Ni-Cd Batteries[4]. Another informative and educative website:[5] *http://batteryuniversity.com/learn/article/recycling_batteries*	Electrodes with CNT or Nano-Phosphate® ($nLiFePO_4$)[6]	In principle during mechanical, chemical or thermal treatment, dependent on the process and on the type of battery with nanomaterial.
Construction and Demolition Wastes.	Reuse of components, sorting of fractions (wood, concrete, brick, metal etc.), metal recycling, secondary building materials, incineration and landfill	CNT, SiO_2, TiO_2, Fe_2O_3, Cu, Ag	During destruction of buildings (dust emissions), shredding, grinding if nano objects are set free. Problem of dispersion of ENM fractions of recycled material

Table 2.A1.1. **Selected waste streams with possible WCNM** *(cont.)*

Waste type	Recycling procedure	Nanomaterials	Theoretically possible sources of nano object emissions in the recycling process
End of Life Vehicles (ELV)	Dismantling for reusable parts (incl. tires), removal of hazardous components (e.g. batteries), shredding and separation of fractions, metals go to smelting and refining, glass is recycled or landfilled, non-metallic shredder residues for incineration or landfill (Ostertag & Huesing, 2007)	CNT, SiO_2, TiO_2 (in plastics, coatings and paints)	Shredding and sorting of fractions, smelting of metals (ENM from coatings), disposal of non-metallic shredder fraction. Modern cars contain electronic components that are normally not removed before shredding, this is a possible source for ENM-emissions
Tires	Collect, storage (danger of ignition), refurbish and reuse, shredding, of metal, reuse of rubber for downcycled products or for energy recovery (according to *www.amni.de/de/anlagen/reifenrecycling.html*) 27% of tires worldwide were recycled 2005, only 6% in 1995; landfill dropped from 62% to 22 % in the same time) Information on Scrap Tires and environmental issues in: *http://en.wikipedia.org/wiki/Rubber_tires#Rubber_tires*	Carbon Black, silica; there are indications that future developments will include others, e.g. CNT, nanoclay (SiO_2) or organic nano-Polymers (ObservatoryNANO 2011)	In principle when shredding, actual tires contain ENMs that are bound to the rubber matrix (Peters 2012)
Recycling of residues from waste incineration:	separation of metals bottom ash from MSWI, (ca. 220 kg of Bottom ash are produced when incinerating 1 tonne of MSW, these contain metal residues (Iron, Aluminium, Copper, even Gold) from MSW. (Fierz and Bunge, 2007, Boeni, 2013)	ENM from WCNM in the municipal waste that are not destroyed or evaporated may stay in the bottom ash	The most efficient recovery of metals from bottom ash is done with dry ash, with dust generation: nano objects can be emitted during pouring, sieving, mechanical and magnetic separation

1. BATREC Industries AG, in Wimmis, Switzerland: *www.batrec.ch/en-us/unser_angebot/batterien/recyclingprozess.html#* (accessed Aug. 28, 2013).
2. *www.batteryrecycling.com/Battery+Recycling+Process* (accessed Aug. 28, 2013).
3. Toxco Recycling Processes, *www.toxco.com/processes.html* (accessed Aug.28, 1013).
4. *www.inmetco.com/services_battery.htm*
5. The Battery University, private project of a former Swiss, now Canadian entrepreneur, founder of CADEX Electronics *http://batteryuniversity.com/learn/article/recycling_batteries* (accessed Aug. 28, 2013).
6. *http://en.wikipedia.org/wiki/Lithium_iron_phosphate#The_Physical_and_Chemical_Properties_of_LFP*

Source: Compiled by authors from sources already cited.

Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 3

Incineration of waste containing nanomaterials

This chapter provides an overview of the emerging scientific findings on the behaviour and exposure of engineered nanomaterials (ENMs) during the waste incineration process and identifies knowledge-gaps regarding specific aspects of the disposal of waste containing nanomaterials (WCNMs). The report includes a brief summary of the scientific information available on the behaviour of ENM during the waste incineration process, an overview of the ENMs of highest relevance in municipal solid waste incinerators (MSWI), a short description of the best available techniques (BAT) of waste incineration and the techniques meant to retain or destroy hazardous substances, as well as a discussion of the possible ways ENMs may pass through existing pollution control devices.

The aim of this document is to provide an overview of the emerging scientific findings on the behaviour and exposure of engineered nanomaterials (ENMs) during the waste incineration process and to identify knowledge-gaps regarding specific aspects of the disposal of waste containing nanomaterials (WCNMs).

This chapter briefly explains the relevance of nanotechnology and provides information on quantities and main sources of ENMs. It then describes waste incineration processes and applicable standards and investigates the fate and behaviour of ENMs. The chapter concludes with a summary of findings and outlook for further investigation.

The report concludes that in order to estimate the quantities of ENMs in waste, the availability of information on ENM containing products on the market is crucial. Moreover, little knowledge is available about the influence and behaviour of ENMs throughout the waste incineration process and currently available literature and findings on incineration of WCNMs are mostly contradictory. Therefore further research is needed. At the current stage, in order to prevent harm for human health and the environment, all waste incineration plants should be equipped with a flue gas treatment system as, for instance, described in the European Union BREF document. In addition, the treatment and disposal of solid residues from waste incineration also require further research.

Relevance of nanotechnology

Nanotechnology is a relatively new and promising field of applications and tasks. ENMs are used for pharmaceuticals, cosmetics, batteries, paints, coatings or as additives in construction materials or other products in order to improve certain properties. The advent of nanotechnology into our everyday lives should therefore not be underestimated. Current research into effects on the environment and human health of the most commonly used ENM shows that some ENMs may be hazardous to human health and the environment, but no nano-specific statement could be made and, thus, exposure evaluation through a case-by-case approach is still recommended (SCENIHR, 2009).

ENMs may also enter the environment at the end-of-life of the products containing them. As nanotechnology is an emerging field, the disposal of WCNMs has raised little attention thus far. Therefore, it is still unclear if an environmentally sound management of WCNMs can be achieved. Consequently, experts fear that ENMs could be released from products and may enter different environmental compounds.

The present report focuses on one waste treatment option – incineration, and the issues surrounding waste containing nanomaterials therein. It includes:

- a brief summary of the scientific information available on the behaviour of ENM during the waste incineration process;
- an overview of the ENMs of highest relevance in municipal solid waste incinerators (MSWI);

- a short description of the best available techniques (BAT) of waste incineration and the techniques meant to retain or destroy hazardous substances;
- a short discussion of the existing hypotheses and suspected ways how ENMs may pass through existing pollution control devices.

Information on waste containing nanomaterials (WCNMs) (quantity, composition)

This section provides some necessary background to the discussion of ENMs in waste incinerators, including quantities of ENMs, the sources of ENMs and the amount of nanomaterials that enter municipal solid waste incinerators (MSWI).

Quantities

The number of waste incineration plants has been increasing over the last few years. According to the OECD (2014), nearly 658 million tonnes of municipal solid waste were generated in the OECD and 145 million tonnes (22%) of those were incinerated in 2012. More detailed figures on the disposal routes of municipal solid waste in the OECD are presented in the Annex.

As mentioned above, the number of products containing ENMs is steadily increasing. Some studies have indicated that, in 2010, TiO2, ZnO, SiO2, FeOx and AlOx dominated the global ENM market by mass flow, mainly used in coatings, paints, pigments, electronics and optics, cosmetics, energy and environmental applications, and as catalysts (Keller et al., 2013). Table 3.1 shows the production quantities of some ENMs worldwide, in Europe, the US and Switzerland. These ENM products become waste when they reach their end-of-life status. For instance, Musee (2011) found that 5000 t/a TiO_2 were produced from 2006 to 2010 and nearly 10 000 t/a between 2011 and 2014. A large, but unknown quantity of these ENMs will end up in waste incineration plants.

Table 3.1. **Summary of engineered nanomaterials (ENMs) produced and used in Europe and in the world**

ENM	Worldwide (t/year) Median and 25/75 percentile	Europe (t/year) Median and 25/75 percentile	US (t/year) Range	Switzerland (t/year) In brackets values extrapolated to Europe
TiO_2	3 000 (550-5 500)	550 (55-3 000)	7 800-38 000	435 (38 000)[a]
ZnO	550 (55-550)	55 (5.5-28 000)		70 (6 100)
SiO_2	5 500 (55-55 000)	5 500 (55-55 000)		75 (6 500)
FeO_x	55 (5.5-5 500)	550 (30-5 500)		365 (32 000)
AlO_x	55 (55-5 500)	550 (0.55-500)		0.005 (0.4)
CeO_x	55 (5.5-550)	55 (0.55-2 800)	35-700	
CNT	300 (55-550)	550 (180-550)	55-1.101	1 (87)
Fullerenes	0.6 (0.6-5.5)	0.6 (0.6-5.5)	2-80	
Ag	55 (5.5-550)	5.5 (0.6-55)	2.8-20	3.1 (270)

The median and the 25/75 percentile are rounded to two significant numbers.

a) The values in brackets for Switzerland have been extrapolated using the population of Switzerland (6.9 Million) and applied to Europe (593 Million)

Source: (Piccinno, et al., 2012; Hendren, et al., 2011; Schmid and Riediker, 2008).

What are the main sources of WCNMs?

There are two main sources from which ENMs enter MSWI. The first one is municipal solid waste (including some residues from manufacturing of ENM containing products). The second source is sewage sludge (SS), if it is incinerated.

Limited information has thus far been made available on products containing ENMs or the quantities such products contain. However, products (e.g. food packaging, cleaning products) containing ENMs have to be disposed of reaching their end-of-life and then enter MSWIs. The same applies to residues from the production of ENMs (Health Council of the Netherlands, 2011).

According to Musee (2011), it can be assumed that 95% of all nanoscale materials contained in cosmetics end up in the wastewater stream. Kuhlbusch and Nickel (2010) verified the release of nanosilver during washing of clothes and textiles containing said ENMs. If wastewater is treated in wastewater treatment plants, the ENMs are transferred mostly into the sewage sludge and therefore in the waste stream. Burkhardt et al. (2010) showed that 93 to 99% of nanosilver is bound in sewage sludge.

Leakage of ENMs into the soil is possible if sewage sludge is used as a fertiliser. In case of energy recovery from sewage sludge, ENMs can enter the incineration plant on that pathway.

How much Nano enters municipal solid waste incinerators (MSWIs)?

Roes et al. (2012) calculated the amounts of ENMs released in MSWI off-gas treatment for 1t of municipal waste, assuming that the content of ENMs in nanocomposites is between 1 wt-% and 10 wt-%. The assumed average content of plastics in municipal solid waste is 12%, of which 7% are nanocomposites. However, it needs to be considered that the average of composites in the MSWI-input can vary strongly depending on local infrastructure and specific waste streams entering the respective MSWI plant.

Waste treatment option: waste incineration

Technical description of a representative MSWI

Most municipal waste incineration plants are equipped with a bunker for waste storage, which usually is a concrete bed. The waste from the bunker is well mixed to enable an effective burn out and is then fed the incineration device. The most common technique for waste incineration is the grate firing system. Thereby a hot and highly-polluted flue gas is produced. This flue gas stream passes through a steam generator for electricity generation. The flue gas then enters the flue gas cleaning system where dust, acids and other harmful substances are eliminated via chemical processes or separated from the flue gas via mechanical processes. The clean flue gas then exits to the atmosphere via a tall chimney, thereby possibly releasing a small amount of ENMs. The residues from the incineration process, called bottom ash, can be used for road construction and other applications in some countries like Germany or have to be landfilled. The residues from the flue gas cleaning system (fly ash), containing ENMs as well, are usually landfilled.

BAT in the OECD and the EU

The use of BAT in waste incineration plants is a complex issue, due to the wide variety of plant constructions, the local and climate circumstances etc. To address this issue, the European Commission has established an information exchange to describe the BAT for various industrial sectors, including waste incineration. The result of this information exchange is the so-called BREF document (best available technique reference document).

According to the BREF document, to prevent harm to human health and the environment, all waste incineration plants should be equipped with a flue gas treatment system. Furthermore, all waste incineration plants in Europe are equipped with a flue gas cleaning system in order to fulfil the requirements of several directives (e.g. Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control, IPPC), OJL 334 of 17.12.2010, p. 17). Moreover, the Directive (2010/75/EU) sets emission limit values and monitoring requirements for gaseous pollutants like dust, nitrogen oxides (NOx), sulphur dioxide (SO_2), heavy metals, dioxins, furans and others. The Directive sets requirements on the release of polluted wastewater leaving the flue gas cleaning facilities. The BREF document on waste incineration, however, does not include any regulations concerning ENMs. It, therefore, can only be used as reference for high quality flue gas treatment in general and standards described within the BREF documents need to be reviewed for their effectiveness removing ENMs. At a subsequent stage, once reliable data is available concerning ENM removal from flue gas of MSWI, the BAT for ENM removal may be included in the BREF-document.

So far only few studies investigated the ENM emissions from MSWI. According to those a high end flue gas treatment system may be able to remove most ENMs from the flue gas. However, this was only shown for certain materials or calculated on a model base.

Therefore, the German Federal Environment Agency/German Federal Ministry of Environment and the German Federal Ministry of Research have already started research projects to study possible emissions of nanoparticles from the incineration process in more detail. However, results are not yet available.

However, still many countries do not implement BAT standard technologies for flue gas treatment. In order to ensure proper flue gas treatment not only with respect to ENMs but all emissions, national governments should enforce high standards for all waste incineration plants.

Fate and behaviour of engineered nanomaterials (ENMs) in waste incineration plants

The fate of ENMs in the MSWI is considerably influenced by redox conditions, the temperature in the waste bed and the post combustion chamber (Roes et al., 2012). These aspects thereby influence the possible emission of ENMs from the MSWI.

Five opportunities exist for the (re-)formation or destruction of ENMs during incineration:

1. ENMs are destroyed due to combustion (for example CNT to CO_2) (Mueller et al., 2013).
2. ENMs are not destroyed or incinerated but captured by the flue gas treatment system (for example metal oxides). These ENMs can be detected afterwards in the fly ash or other residues.
3. Certain types of ENMs may not be destroyed during combustion. However, they react with other substances and form new particles (e.g. $CaCO_3$ to CaO and CO_2 or ZnO + HCL give $ZnCL_2$ + H_2O).

4. Bigger particles decompose and turn into new, smaller particles or even ENMs. Roes et al. (2012) describes how ENMs can be destroyed and, converted into other ENMs or left unchanged during incineration.
5. Agglomeration of ENMs to bigger particles may occur, therefore, those particles lose their “nano” status.

The present report focuses on the first two cases. In order to fill the knowledge gaps about the fate of ENMs in waste incineration plants more research is necessary. The German Federal Environment Agency has commissioned a study analysing the fate of nanoscaled TiO_2 within a waste incinerator and a sewage sludge incineration plant. Within this study, a mass balance will be conducted. Results will be available in 2015. France has also launched two research projects in order to assess the emissions from incinerating WCNMs and the effectiveness of flue gas treatment systems. Results will be available in due course.

In 2012, a survey was published which focused on the incineration of ENMs in real waste incineration plants. Walser et al. (2012) analysed the behaviour of cerium oxide (hydrodynamic average 80 nm) during incineration.

This considered two cases: in the first case, ENMs were introduced by spraying them onto the waste. In the second case, ENMs were injected directly into the furnace. The mass balance of the first case showed that nearly 81% of ENMs were transferred into the slag, nearly 19% into the fly ash, 0.02% into the quench water and only 0.0004% into clean flue gas. In the second case 53% of ENMs were found in the slag, 45% in the fly ash and 1.7% in the quench water.

Walser et al. (2012) concluded that electrostatic precipitators, in combination with a wet flue gas purification system, can effectively remove nanosized oxides from the flue gas stream. Therefore, no nano-CeO_2 will be emitted from waste incineration plants equipped with such a flue gas treatment.

In contrast Roes et al. (2012) stated that the removal efficiency for particles from the flue gas is very high for particles larger than 100 nm. For particles smaller than 100 nm the removal effectiveness is supposed to be reduced significantly. ENMs smaller than 100 nm are partially removed by fabric filters and wet scrubbers, but a significant amount (up to 20%) may pass through such devices. The ENMs captured by the scrubbing system end up in the residues (bottom ash and fly ash). Roes et al. (2012) concluded that leaching from these residues should be prevented. However, it should be mentioned that the efficiency depends on the filter technique as well as on the filter material and can vary from plant to plant. Moreover, this study included no experiments and results are based on theoretical considerations only.

Mueller et al. (2013) found that the majority of ENMs enter bottom ash during incineration and end up in landfill sites as part of bottom ash. Other residue flows, such as fly ash, are of a smaller magnitude than bottom ash.

Mueller et al. (2013) concluded that waste incineration can have an important influence on some ENMs. Most ENMs are supposed to end up in the incineration residues and thus mostly in landfills but carbon nanotubes (CNT) for example may behave differently as models indicate that they may be burnt with an efficiency of 94% due to their chemical nature. However, some of the available data indicates that carbon nanomaterials may not incinerate as efficiently as expected (Vejerano et al. 2014).

Mueller et al. (2013) also estimated a total of 80 000 t/a of fly ash that are produced in waste and sludge incineration plants in Switzerland. According to their measurements, a fraction of only 0.00058 wt-% of the sludge and waste incineration fly ash is smaller than 100 nm corresponding to a total of 464 kg per year. Differing from that, results from the calculation model used by Mueller et al. (2012) in a different study are nearly 50 times higher: 22 t/a TiO_2, 0.8 t/a ZnO, 160 kg/a Ag and 4.9 kg/a of CNT. Similarly, Buha et al. (2014) investigated five waste incineration plants in Switzerland with electrostatic precipitators or bag-house-filters and reviled that a range of 0.00009% to 0.07% of the fly ash in mass based volumes were identified as nanomaterials. They also suggested that ENMs may form a decent proportion of nanomaterials found in the flue gas through comparison with modelling results. The reason given for the discrepancy between measured and modelled values is that ENMs tend to agglomerate and quickly form bigger particles of several hundred nanometres. Therefore, they are no longer ENMs, according to the recommendation of the European Commission.

The European Commission declared that the open burning of textiles containing CNTs could emit such ENMs. It is assumed that only incineration above 850°C can eliminate CNTs. Therefore, incineration in modern and well-operating waste incineration plants is necessary, where such high temperatures can be reached (European Commission DG Environment, 2009).

The Health Council of the Netherlands (2011) noted that although MSWI emit ultrafine particles they are negligible in comparison to the emissions from road traffic. The concentration of fine particles are reduced by a factor of one thousand after scrubbing the flue gas, but still a high number of fine particles may not be captured by scrubbing and, thus, emitted to the air. The Council concluded that it is quite plausible, based on such a limited body of evidence, that the waste incineration process releases ENMs.

Summary and outlook

The number of products containing ENMs will probably increase in the future. As a result, the amount of waste containing ENMs will also increase. Information about the influence of the ENMs embedded in products is scarce. In order to estimate the quantities of ENMs in waste, the availability of information on ENM-containing products on the market is crucial.

Moreover, little knowledge is available about the influence and behaviour of ENM size throughout the waste incineration process. The available literature and the findings on incineration of WCNMs are mostly contradictory. On the one hand, there are studies reporting that measurements in a waste incinerator show no emission of ENM; on the other hand, model calculations find that ENMs can pass through cleaning devices. Therefore, further research is needed and has partly been started.

However, in order to prevent harm for the human health and the environment, all waste incineration plants should be equipped with a flue gas treatment system as described in the BREF document. From the only studies available at the moment it can be assumed that, if a plant is equipped with a BAT flue gas treatment system, the majority of ENMs will be captured by the treatment system. However, this was only shown for nano-$CeO_{2;}$ all other estimations were based on theoretical considerations. Additionally, all incineration parameters such as temperature, residence time or oxygen level should be taken into consideration in order to achieve a high level of ENM destruction and ideal conditions for ENM removal.

Unfortunately, there are still a large number of waste incineration plants worldwide that do not have adequate flue gas treatment systems, not only concerning ENMs but all other emissions as well. National governments should therefore ensure high standards in flue gas treatment systems of MSWI plants in general.

The understanding of ENM behaviour during municipal solid waste incineration and how ENMs are released into the environment is at an early stage. In order to learn more about this and to improve data availability, a more detailed survey of different ENMs in various waste incineration plants and co-incineration plants is necessary. Such studies should include determining the conditions that enable the efficient removal of ENMs from MSWI flue gas. Furthermore, the fate of ENMs in the solid residues from waste incineration plants also needs further research and should not be disregarded.

References

Buha, J., et al. (2014), "Physical and Chemical Characterization of Fly Ashes from Swiss Waste Incineration Plants and Determination of the Ash Fraction in the Nanometer Range", *Environmental Science &Technology*, Vol. 2014, No. 48, pp. 4765-4773.

Burkhardt, M., et al. (2010), "Verhalten von Nanosilber in Kläranlagen und dessen Einfluss auf die Nitrifikationsleistung in Belebtschlamm (Behavior of nanosilver in sewage treatment plants and its influence on nitrification in activated sludge)", Environmental Sciences Europe, Vol. 22, No. 5, pp. 529-540.

European Commission DG Environment (2009), *How Nanotubes Could be Released Into the Environment*, Original source: Köhler et. al. (2008), "Studying the Potential Release of Carbon Nanotubes Throughout the Application Life Cycle", Special Issue 12, Newsletter.

Health Council of the Netherlands (2011), *Nanomaterials in Waste*, The Hague: Health Council of the Netherlands, publication no. 2011/14E, *www.gezondheidsraad.nl/sites/default/files/Nano_waste_201114E.pdf*.

Hendren, C. et al. (2011), "Estimating Production Data for Five Engineered NMs as a Basis for Exposure Assessment", Environmental Science &Technology, Vol. 45, No. 7, pp. 2562-2569.

Keller, A.A. et al. (2013), "Global life cycle releases of engineered nanomaterials", *Journal of Nanoparticle Research*, Vol. 15 No. 6.

Kulbusch, T. and C. Nickel (2010), *Emission von Nanopartikeln aus augewählten Produkten im Lebenszyklus (Emission of nanoparticles from selected products during their life cycle)*, Institut für Energie und Umwelttechnik (IUTA) e.V.,Bereich „Luftreinhaltung & Nachhaltige Nanotechnologie (Institute for Energy and Environmental Technology (IUTA) eV, The "Air Quality & Sustainable Nanotechnology") (funded by German Umweltbundesamt UBA), On behalf of the Federal Environment Agency (Germany), Duisburg.

Mueller, N. et al. (2012), "Nanomaterials in Waste Incineration and Landfills", Internal Empa-report, *www.empa.ch/plugin/template/empa/*/124595*.

Mueller, N.C. et al. (2013), "Modelling the Flows of Engineered NMs during Waste Handling", *Environmental Science, Processes & Impacts*, Vol. 15, pp. 251-259.

Musee, N. (2011), "Nanowastes and the Environment: Potential New Waste Management Paradigm", *Environment International*, Vol. 37, pp. 112-128.

OECD (2014), "OECD Waste Statistics", *OECD Environment Statistics*, *http://stats.oecd.org//Index.aspx?QueryId=51347*.

Piccinno, F. et al. (2012), "Industrial Production Quantities and Uses of Ten Engineered NMs in Europe and the World", *Journal of Nanoparticle Research*, Vol. 14, No. 9, pp. 1109- 1120.

Roes, L. et al. (2012), "Preliminary Evaluation of Risks Related to Waste Incineration of Polymer Nanocomposites", *Science of the Total Environment*, Vol. 417-418, pp. 76-86.

SCENIHR (2009), “Risk Assessment of Products of Nanotechnologies”, Scientific Committee on Emerging and Newly Identified Health Risks, European Commission, DG Health & Consumers, Brussels, *http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_023.pdf*.

Schmid, K.and M. Riediker (2008), “Use of Nanoparticles in Swiss industry: a Target Survey”, *Environmental Science &Technology*, Vol. 42, No. 7, pp 2253-2260.

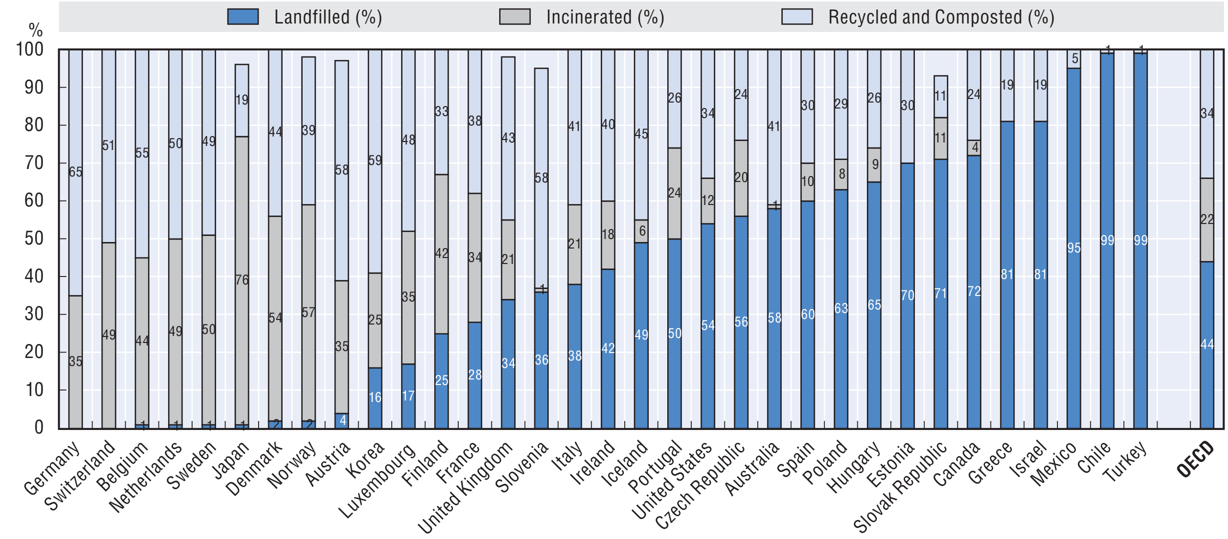
Vejerano, E.P. et al. (2014), “Characterization of Particle Emissions and Fate of Nanomaterials during Incineration”, *Environment Science Nano*, Vol. 2014, No. 1, pp. 133-1431.

Walser, T. et al. (2012), “Persistence of Engineered Nanoparticles in a Municipal Solid Waste Incineration Plant”, *Nature Nanotechnology*, Vol. 7, pp. 520-524.

ANNEX 3.A1

Disposal routes of municipal solid waste

Figure 3.A1.1. **Disposal routes of municipal solid waste in the OECD in 2013**



Notes: The data is as of 2013 or the most recent data available for each country since 2009. No data was available for New Zealand. The sum of the categories presented here might not add up to 100% because other recovery and other disposal treatments are not presented.

Source: OECD (2016), "Municipal waste", OECD Environment Statistics (database), *http://dx.doi.org/10.1787/data-00601-en* (Accessed on 19 January 2016).

Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 4

Landfilling of waste containing nanomaterials and nanowaste

This chapter provides an initial review of available scientific information about the sources of ENMs in landfills, their fate and behaviour there, as well as the effectiveness of landfills in retaining ENMs. It investigates potential pathways of ENM releases into the environment and considers the related risks. The chapter summarises key points of concern and identifies existing knowledge gaps.

The nanotechnology industry is rapidly generating new forms of waste streams due to the production and use of engineered nanomaterials (ENMs) and their use in nanoproducts; however there is limited literature on the fate, behavior and impacts of these waste streams on the environment and human health. This growing industry, increasing in both production rates and diversity of products, will lead to an increase of ENMs in waste management facilities through the treatment of end-of-life consumer and commercial products (waste containing nanomaterials). Several studies have indicated that a significant proportion of ENMs may be disposed in landfills and have suggested that priority attention should be paid to improving the understanding of these waste streams, the associated environmental risks and the effectiveness of current waste management practices and technologies. This is required in order to prevent potential pollution by nanomaterials (Asmatulu et al., 2012; Bolyard et al., 2013; Boldrin et al. 2014; Bystrzejewska-Piotrowska et al., 2009; Keller et al., 2013; Holden et al., 2014; Lin et al. 2010; Lozano and Berge, 2012; Mueller and Nowack, 2008; Musee, 2010; Nowack et al., 2013; Yang et al., 2013).

The purpose of this report is to provide an initial scoping review of readily available scientific information about the source of ENMs in landfills, their fate and behavior in landfills, and the effectiveness of treatment technologies. As with other potential pathways of ENM release to the environment, there are many complex factors to consider. This is an area of emerging scientific research with on-going investigation and debate within the field of nanotoxicology. This includes defining the characteristics of ENMs and their potential toxicity which can vary as a function of both their chemical composition and other characteristics including shape, size, and structure. Additionally, it is also quite likely that a large fraction of ENMs will transform once released, which needs to be taken into consideration (Keller et al., 2013). Although all ENMs may not be considered to be hazardous (RCEP, 2008), the scientific literature consistently discussed risks associated with ENM disposal in landfills from a context of precaution. In presenting their findings, this report included those precautionary views, accordingly which may be validated or disproved as additional scientific studies are made available. Finally, the report intends to provide a basis for discussion by summarising key points of concern and identifying knowledge gaps in order to improve decision-making concerning the management of ENMs in landfills.

Landfills and the introduction of nanomaterials in waste

Waste disposal on land (dumping) and landfilling remain the most prominent waste management techniques used worldwide. The standards and practices for this type of waste disposal vary greatly ranging from uncontrolled sites to highly specialised and controlled engineered landfills. The potential release of contaminants through landfill gas and leachate is largely dependent on landfill design, site conditions and the sophistication of the control measures in place, including landfill gas recovery and leachate collection and treatment systems.

Modern engineered landfills use synthetic barriers, with few relying on natural barriers, to line the bottom of a landfill and incorporate collection systems for both leachate and landfill gas. The purpose of these collection systems is to capture and treat leachate and landfill gas; thereby preventing the migration of leachate into ground/surface water and the release of untreated landfill gases to the atmosphere. An un-engineered landfill would be considered an uncontrolled system due to the lack of environmental controls, potentially resulting in significant environmental exposure of contaminants.

Because of the widespread use of ENMs in a broad range of products, it is possible that some ENMs could be released through landfill gas; however this report will primarily focus on ENMs that may be present in landfill leachate, as this is considered to be the primary means by which ENMs could be transported out of a landfill. Characterisation of landfill gases to identify the presence of ENMs should be considered an important area for further research.

Landfill leachate is generated when rain passes through the waste mass and by the liquid generated due to the breakdown of waste within the landfill. The composition of leachate is extremely variable depending on the type of waste landfilled, the quantity of precipitation, the construction and operation of the landfill, the age of the landfill and other factors such as pH, temperature and microbial populations. The variability of leachate chemical composition is also influenced by the diversity of chemical substances contained in consumer products found in residential wastes from households and other wastes disposed in landfills. A variety of other wastes disposed in landfills can originate from light industrial, commercial and institutional activities and may include construction, renovation and demolition waste; contaminated soils; ash and sewage sludge, which may also be sources of ENMs (see section 4.2.1).

Landfills remain a topic of intensive research with international scientific studies (Kurniawan, 2006; Eggen et al., 2010; Marcoux et al., 2013) voicing concern about the potential environmental impacts of releases of contaminants from landfills. As part of a multi-year research program (2008-13) in Canada, key macroscale[1] chemical substances were detected in leachate samples from a select number of large municipal solid waste landfills. Research findings demonstrated that conventional on-site treatment technologies and wastewater treatment technologies may not be effective in treating some substances found in landfill leachate under various conditions (Marcoux, et al., 2013; Conestoga-Rovers & Associates, 2013). This study did not include ENMs, but demonstrates the variability of treatment efficacy. A recent study by Hennebert et al. (2013) determined the presence of ENMs in varying waste leachates, demonstrating that a significant amount of colloids (dispersed phase in the size range of 1nm-1µm) in leachate were found, different in elemental composition from natural ones.

While many of the substances detected in leachate are often not found in high concentrations, little is understood about the potential for synergistic effects of this multi-contaminant source of pollution nor have all possible substances been exhaustively analysed. The disposal of ENMs in landfills may add a level of unanticipated complexity, uncertainty and risk to waste management systems which are not designed to cope with all existing contaminants (Marcoux, et al., 2013). Although effective in treating a variety of substances, conventional on-site leachate treatment systems may, in some cases, not be effective in removing certain chemical substances or ENMs under varying conditions. Therefore, it is pertinent that the risks of ENMs in landfills and potential for releases are identified, including downstream impacts on environmental and human health. This information is required to guide future waste disposal management decisions and the development of solutions.

Source of nanomaterials in landfills

ENMs are used in a range of product innovations in the consumer, industrial and medical sectors and have been incorporated in cosmetics and personal care products, clothing and textiles, antibacterial agents, polishing cleaning and binding agents, solar cells, strong-lightweight plastics for the automotive and aircraft industries, preservatives, food processing and food packaging (Bolyard, 2011, Health Council of the Netherlands 2011, Musee, 2011). The Project on Emerging Nanotechnologies (2014) reported that 1628 nanoproducts were in use as of October 2013, with the largest category consisting of health and fitness products (48% of all nanoproducts) of which cosmetics and personal care products represent the largest proportion (37%) of this sub-group. It is beyond the scope of this report to determine which nanoproducts (and/or key ENMs) are primarily disposed of in landfills, characterise their risk or quantify ENM flows to landfill. However, this work has been initiated by several researchers. The continuation of these investigations, including ENM classification and hazard identification, will serve to guide further research on which ENMs are found in landfills and also identify their potential risk.

The BSI (British Standards Institution) British Standards Guide PD 6699-2 identifies four main types of nanomaterial-related waste streams (solid and liquid):

- pure nanomaterials;
- items contaminated with nanomaterials, such as containers, wipes, disposable Personal Protective Equipment (PPE);
- liquid suspensions containing nanomaterials;
- solid matrices with nanomaterials that are friable (can easily crumble or pulverise) or have a nanostructure loosely attached to the surface, such that they can reasonably be expected to break free or leach out when in contact with air or water, or when subjected to reasonably foreseeable mechanical forces (BSI, 2007).

A key source of ENMs in municipal landfills is the disposal of ENMs present in consumer products at the end of their useful life (Asmatulu et al., 2012; Boldrin et al. 2014; Ganzleben et al., 2011; Keller et al., 2013; Reinhart et al., 2010; Nowack et al, 2013). One life-cycle analysis estimated that over 50% of three commonly used ENMs produced by weight (nano-silver, nano-titanium dioxide and carbon nanotubes) will eventually end up in landfills (Mueller and Nowack, 2008). Another study by Keller et al. (2013) estimated that the majority (63-91%) of over 260 000-309 000 metric tonnes of global ENM production in 2010 will likely be disposed of in landfills. In terms of ENMs used by weight, the largest source of nanoproducts may be those used in plastic composites and building materials (Bottero et al., 2015; Keller et al., 2013).

The disposal of nanowastes from industrial sources into regulated hazardous waste landfills and potentially municipal landfills should not be overlooked. For example, according to information obtained by the Royal Commission on Environmental Pollution (2008), it was stated that in one process of the manufacturing of fullerenes (carbon based ENMs), only about 10% of this material is usable and the rest are disposed of in landfills. Boldrin et al. (2014) also points to data indicating that the amounts of waste generated from the manufacturing processes are, in several cases, significantly larger than the amount of the final ENM product. However, this may not be indicative of other ENM manufacturing processes and is likely a worst case scenario considering the economic implications of discarding a high proportion of the product. Although not conclusive, this indicates that the handling of nanowaste streams from ENM manufacturing should also be considered a priority (Boldrin et al. 2014).

In addition to these sources, incinerators and wastewater treatment plants may also transfer ENMs to a landfill through the disposal of ash, slag or biosolids. Nanoparticles that are retained and or transformed during sludge stabilisation or incineration could then enter landfill leachate (DiSalvo et al., 2008; Mueller et al., 2012). Although it is possible to incinerate waste without releasing nanoparticles into the atmosphere, observations have shown that residues to which they bind are eventually disposed in landfills (Walser et al., 2012). Mueller et al. (2012) estimated the flow of ENMs in waste streams in Switzerland and their modeling found that the major ENM-flow goes from the waste incineration plant as bottom ash to landfills. Biosolids could also be a significant source of ENMs to landfills. It is estimated that about ¾ of the total nano-titanium dioxide entering wastewater treatment plants would finally end up in landfills and that an average of 4.77 tonnes of nano-silver may be dumped into landfills per year (Mueller and Nowack, 2008). Another source of nanowaste requiring consideration is the use of ENMs in remediation, for the removal of pollutants from either aqueous effluents and/or gas. These generate another form of nanowaste needing to be disposed of properly, after they have been used for remedial purposes (Gao et al., 2008).

In summary, ENMs contained in a large diversity of consumer nanoproducts, nanowastes from manufacturing and from remediation, as well as residual waste products from other waste management systems are disposed of in landfills. As the likely final destination of many ENMs (Keller et al., 2013; Kim, 2014), landfills require special attention. Further research is required to determine the extent to which landfills act as a final repository for ENMs or as a pathway of ENM exposure to the environment.

What factors contribute to the risk and complexity of disposing nanomaterials?

ENMs exhibit distinctive "footprints" as a result of their inherent chemical composition, shape, size and structure, resulting in unique behaviors in different environmental media even when fabricated from the same bulk parent material (Pal et al., 2007). The risk to the environment is not soley based on quantity or mass (concentration) but also on the unique properties of nanomaterials and their behavior (Ganzleben et al., 2011). These considerations, in addition to the following factors, require careful deliberation for landfill disposal of ENMs or products containing ENMs:

i) **The manufacturing of ENMs may generate "nano by-products" and other nanowaste streams with distinct toxicological characteristics requiring specialised disposal.**

Templeton et al. (2006) studied the interactions of SWCTs (single-walled carbon tubes) on crustacean test species and found that, though the original purified SWCTs caused no detrimental effects in the test species, their by-products (a synthetic byproduct during arc-discharge synthesis) could potentially cause deleterious effects. The finding of significant toxicity from a nanomaterial manufacturing byproduct stresses the need for considering such materials in any assessment of environmental and health effects of these ENMs (Templeton et al., 2006).

Additionally, the manufacturing of a single ENM may generate nanowaste streams of different forms with variant hazard levels. For example there are 10 major types of MWCTs (multi-walled carbon nanotubes), which can be produced using 5 different fabrication techniques (some types containing varying degrees of impurities), with varying nanostructure sizes using 3 different purification techniques and 10 possible surface coatings (used to maintain their nanoscale properties during their application) (Musee, 2010).

ii) **A given nanoproduct may pose a range of risk profiles upon disposal.**

Risk is evaluated by identifying both the inherent hazard of an ENM and potential exposure to environmental or human receptors. For example, an ENM considered highly hazardous, but firmly embedded in a product matrix (with low or no possibility of exposure) will likely present a low risk. However, an ENM, loosely bound within a personal care product such as sunscreen, may present risks upon disposal ranging from low to high depending on the differing toxicity of the ENMs used in their production (nano- titanium dioxide, nano-zinc oxide or fullerenes) (Musee, 2011) and/or depending on their surface formulations (Botta et al., 2011). Therefore ENMs must be examined in the context of the product matrix, formulations and their use and application in order to determine the most appropriate method for disposal.

iii) **ENMs may bond with pollutants enhancing their toxicity and may facilitate faster translocation of these pollutants through air, soil and water.**

The sorption of pollutants onto ENMs may increase the toxicity, transport (Farré et al. 2009) and in some cases increase the bioavailability of pollutants. He et al. (2012) found that in addition to organic molecules, potentially toxic metal ions also have the ability to adsorb on the nanoparticle surface, increasing the transport and toxicity effects of metal atoms (prompting the use of ENMs in remediation of toxic metal pollutants). This finding was also reported by Gao et al. (2008), whose results found that mercury sorbed onto ENMs could become bioavailable and toxic if introduced into natural environments. Cheng et al. (2004) and Yang et al. (2006) also reported that organic compounds such as polycyclic aromatic hydrocarbons (PAHs) can be adsorbed onto carbon nanotubes causing an enhancement of PAH toxicity. However, there are also some instances where ENMs may decrease the toxicity of substances (Baun et al., 2008).

Because of their small size and slower rate of gravitational settling, some ENMs may remain suspended in air and water for longer periods. They may be readily transported over much greater distances than larger particles of the same material (Lin et al., 2010). Depending on the properties of the ENMs and soil, ENMs may be retained by soil particles or break through the soil matrix and reach groundwater (Lin et al., 2010). Soils with high clay content tend to stabilise ENMs and allow greater dispersal (US EPA, 2014). However, Lecoanet et al. (2004) reports that ENMs exhibit widely differing transport behaviors.

iv) **The increase in concentrations of ENMs in the environment may cause long-term chronic effects through different food chains.**

Some ENMs can persist for a long time or be taken up by biological organisms and can act as an ecotoxicological hazard, undergo biodegradation or bioaccumulate in the food chain causing long-term chronic effects (Edouk et al., 2013; Lin et al., 2010; SCENIHR, 2006). Toxicity to food web members have been reported for bacteria, plants and multicellular aquatic and terrestrial organisms (Holden et al., 2014, Lui et al., 2014, Maurer-Jones et al., 2013). In addition, the adsorptive capabilities of some ENMs and their ability to permeate across membranes raises concerns regarding the transport of toxic chemicals in tissues and cells (Musee, 2011). This is of interest because though certain ENMs may not be toxic, if the nanowaste mixes/interacts with other conventional waste streams containing toxic chemicals, the former may act as a Trojan horse to transport the latter into the cell (Limbach et al., 2007). However, the quantity of ENMs which can act as a Trojan horse for other contaminants, after their transformation, will depend on competition between ENM surfaces and other surfaces (Auffan et al., 2012).

When disposing of various nanoproducts, nanowastes and by-products of ENM manufacturing, the unique physicochemical properties of ENMs found in a diversity of products with variant hazard levels, requires careful consideration. The potential for interactions between ENMs with other contaminants in leachate, which then could have an impact on the toxicity and dispersion of contaminants beyond the landfill, requires further investigation. These factors, in a worst case scenario, could contribute to potential widespread contamination of the environment. Failure to adequately address landfill waste disposal management concerns may allow the release of ENMs (to water, air, and soil), which may cause contamination of soils as well as surface and underground water resources (Musee, 2011), particularly from un-engineered landfills. This subject is currently being studied by the European Union (EU), the United States (US) and France-ANR (Agence Nationale de la Recherche).

Fate of nanomaterials in landfills

It is likely that changing in-situ landfill conditions will greatly influence ENM behaviour and need to be considered when determining the fate of ENMs since as they age, their surface changes and reactivity is altered (Reinhart et al., 2010). Landfills remain anaerobic over time; however other conditions such as pH generally increase in older landfills. Landfills also exert physical stressors to waste through abrasion and compaction of the waste to reduce its volume. Given this context, the release of ENMs incorporated in nanoproducts is probable within a landfill (Reinhart et al., 2010; Lozano and Berge, 2012; Nowack et al., 2013). The fate of ENMs will most likely be a function of the mobility of the nanoparticles, their degradability and the degradability of the host material (Hansen, 2009). Physicochemical and hydrological conditions in the landfill may affect both the matrix material and the transformation of ENMs themselves (Boldrin et al., 2014).

Are nanomaterials subject to degradation in landfills?

There is discussion in the scientific literature that indicates that some ENMs may be subject to degradation and/or that they may be released from a nanoproduct under landfill conditions, depending on the nature, location and quality of the ENM bonds. The potential ease of ENM release from a given product is a function of loci (placement) in the nanoproduct (Hansen et al., 2008). However, this is to be verified through continued research. This is currently one aspect of research under *The NanoRelease Project*, based in the United States[2], which aims to support the development of methods to understand the release of ENMs used in products and foster the safe development of ENMs (ILSI, n.d.). Other related research projects in Germany, include FRINano[3], CarboSafe[4], CarboSave and CarbonLifeCycle[5].

Generally, ENMs firmly bound in a solid nanoproduct (such as in automobile parts, memory chips etc.) may exhibit no or a very low degree of exposure (to the environment or living organisms), as the ENMs typically remain within the product. However, even with a more firmly bound product, harsh environmental conditions within landfills, such as low pH and strongly reducing conditions (due to the anaerobic environment), will likely aid the release of ENMs bound in polymers (Reinhart et al., 2010). Materials bound in plastics/ plastic resins/polymers/metal products, such as those found in construction waste, may also be released into the leachate as a result of mechanical stress and abrasion during compaction (Mueller et al., 2012; Nowack et al., 2013) and/or contact with leachate of an aggressive nature (Lozano and Berge, 2012).

In a study of the potential release of carbon nanotubes (CNT) used in composites, Nowack et al. (2013) discuss the possibility that if CNT composites are landfilled, they could slowly breakdown depending on their degradability and potentially release ENMs to the leachate (or via dust from weathered composites). However, degradation of the polymer matrix, under conditions in engineered landfills, and release of CNTs is likely to be extremely slow. In contrast, the situation in an un-controlled landfill may lead to greater post-consumer and environmental releases of discarded CNT composites (Nowack et al., 2013).

Conversely, ENMs freely bound or loosely bound in liquid suspensions, potentially will have a high to very high degree of exposure (Musee, 2011). For example, release of ENMs from discarded products such as cosmetics, sunscreens, hair products, wastewater biosolids and nanomaterial manufacturing wastes may occur. Once nanomaterials are released into the leachate, leachate composition will significantly influence material fate (Lozano and Berge, 2012). Boldrin et al. (2014), applied an exposure assessment framework for titanium dioxide (TiO_2) used in sunscreen and states that, considering the significant amounts of cosmetics containing ENMs which may be disposed of, potential exposure is defined qualitatively as “medium”. However, it is important to consider that many nanoparticles are subject to important speciation modifications (or transformation) as they are released from the initial products (Kaegi et al., 2011). ENMs may aggregate and agglomerate to form larger particles losing their inherent nano properties.

ENMs embedded within a product matrix, on the surface of a product or freely suspended particles in a product, will affect the potential for nanoparticle release from a product. Landfill conditions (chemical and physical) could favor the release of nanoparticles from solid waste nanoproducts, although personal care products or other loosely bound ENMs in liquid form could potentially be more problematic and available to react with leachate and its chemical components (Lozano and Berge, 2012; Reinhart et al., 2010). Further research and hazard experiments, are required to study ENMs and their potential transformation under different environmental conditions, including landfills to accurately predict their effects.

How will leachate characteristics influence nanomaterials and their transport?

Studies have reported that organic matter in leachate influences ENM stability, aggregation and transport, and other findings discuss the influence of pH and other factors on ENM solubility and aggregation. However, leachate (a colloidal system) is very complex, and this report is not intended to provide an in-depth scientific analysis of the topic. The transformation of ENMs after their release in the environment is currently being undertaken by research programs such as the FP7 NMP (NanoMaterials Programme), NanoSUN (sustainable nanotechnologies) and NanoMILE (Engineered nanomaterial mechanisms of interactions with living systems and the environment: a universal framework for safe nanotechnology).

One study on ENMs and pH found that the stability of nanoparticles in water depends upon their chemical structure, water pH and temperature (DiSalvo et al., 2008). The results demonstrated that with fullerenes (C_{60}) the more alkaline the water, the less aggregation occurred where the diameter of C_{60} aggregates decreases with an increase in pH. However in a study by Labille et al., (2010) on the aging of TiO_2 nanocomposites (coated or encapsulated) used in sunscreen, depending on solution pH, ionic strength and natural organic matter (NOM) concentration, the colloids tend to aggregate and settle out of the water column (Labille et al., 2010). Additionally, Gao et al. (2008) discuss how ENM adsorption to pollutants is dependent on pH. The adsorption onto a solid depends effectively on the pH, but in a complex medium such as leachate, there is competition for many other sorbents and pH is not the main factor (Bottero et al., 2015). At low pH values, metallic ENMs become positively charged (+), whereas at high pH the charge becomes negative (-). The pH at which the surface of the ENM becomes neutral is called the isoelectric point (IP) and particles are expected to agglomerate (Gomez-Rivera, 2011). Another factor to consider is ENMs are often coated with engineered organic substances, which act to keep particles evenly suspended in the product. This has several implications for aggregation behavior (von der Kammer et al., 2014).

Several studies have reported on the interaction between organic matter in leachate and its influence on ENM transport. Organics typically found in mature landfill leachate, such as humic and fulvic acid, have been reported to stabilise ENMs (Hyung and Kim, 2008; Saleh et al., 2010; Lin and Xing, 2008). This enhanced stabilisation reduces particle aggregation, generally correlating to greater material mobility (Petosa et al., 2010). Jaisi et al. (2008) and Lozano and Berge (2012) reported that transport of SWCNTs (single-walled carbon nanotubes) is enhanced in the presence of humic acid. Similarly, Lin and Xing (2008) reported that tannic acid improves mobility of carbon nanotubes. Enhanced mobility of MWNTs (multi-walled carbon nanotubes) when in the presence of natural organic matter was also reported by Saleh et al. (2008). Research results at the University of Central Florida suggested that humic acid could mobilise ZnO nanoparticles in leachate, thus making them more susceptible to transport (Bolyard et al., 2012). The study conducted by Lozano and Berge (2012) concluded that even at high ionic strengths, humic acid creates a steric barrier to material aggregation/agglomeration, which likely aids the transport of the materials through the waste.

Generally, pH could be one factor, among others (such as ionic strength, temperature, NOM, specific ENM properties etc.), which can influence whether an ENM aggregates in solution, but may promote or inhibit aggregation under different conditions (in conjunction with other factors) (Liu et al., 2014). In terms of the presence of humic acid or other organic matter specifically found in leachate, results indicate that the stabilisation of ENMs may occur, minimising aggregation and reducing precipitation. Conversely, humic acid or fulvic acid could limit the transport of ENMs if their affinity for the background is stronger than ENMs (Bottero et al., 2015; Lowry, 2012). A reduction in the deposition rate of ENMs within landfills may increase the maximum travel distance of many different types of ENMs. However, this is not conclusive and requires further investigation.

Will nanomaterials influence microbial processes?

Generally, Holden et al. (2014) discuss the concern that ENMs can decrease bacterial diversity in the environment with potential negative impacts on both ecosystem and human health. A few studies have specifically looked at the antimicrobial or antibacterial properties of ENMs within landfills and other findings, used only for a basis of comparison, discuss how these antibacterial properties of ENMs potentially alter the functionality of micro-organisms used in treating wastewater, especially in biological treatment plants (Klaine et al., 2008; Holden et al., 2014). In some countries, landfill leachate is primarily treated by wastewater treatment plants and therefore ENMs in leachate could have an indirect impact on the effectiveness of the treatment process.

ENMs exert anti-microbial properties through different mechanisms such as the formation of reactive oxygen species (ROS) and disruption of physiological and metabolic processes (Edouk et al., 2013). One specific study relating to the impact of ENMs, namely nano-silver (nAg), and its influence on the microbial process in landfills was reported by Yang et al. (2013). The study reported the inhibition of methanogenesis (generation of methane) and biogas production from municipal solid waste (MSW) due to the presence of nano-silver at a concentration of 10 mg/kg, although they found no impact for lower concentrations. Another study conducted at the University of Central Florida produced results suggesting that zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles did not have an inhibitory effect on anaerobic or aerobic processes when exposed to mature or middle aged leachate due to the low concentration of dissolved/soluble zinc (Bolyard et al., 2012).

Other sources voice concern that the antibacterial properties of many metal ENMs may considerably affect the operation of wastewater treatment plants, allowing conventional chemical and biological contaminants to potentially pass untreated through after microbial functionalities have been compromised by the presence of ENMs (DiSalvo et al., 2008; Health Council of the Netherlands, 2011; Klaine et al., 2008; Musee, 2011). However, this may only occur with high concentrations of ENMs. Results from a study conducted by Hou et al. (2012) indicated nano-silver (referred to AgNPs in this study) at a concentration of up to 0.5mg L^{-1} would not dramatically impact the NH_4 (ammonium) removal efficiency of the activated sludge process. Yang et al. (2013) suggest that the release silver ions of (Ag^+) from nano-silver in wastewater may inhibit nitrification (conversion of ammonia (NH_3) to nitrate (NO_3) by bacteria) and that nano-zinc oxide (ZnO) and nano-titanium dioxide (TiO_2) could decrease nitrogen and phosphorus removal efficiencies at high concentrations. Nitrification is also an important component of treating leachate in on-site landfill biological treatment systems, which are used to eliminate soluble organic pollution using microorganisms (bacteria) (WSP Canada 2014).

Based on this information certain ENMs particularly with metallic and metal oxide nanoparticles, may have the potential to inhibit microbial treatment processes of landfill leachate treatment systems (and in wastewater) at high concentrations, although several variables exist that may influence whether or not microbial functions will be affected. This may include how the variable constituents of leachate interact with ENMs, their concentration, whether the conditions are aerobic or anaerobic and whether the ENMs exhibit antibacterial properties before and after transformation. This area will require further investigation.

Do nanomaterials penetrate landfill liners?

Landfill liners are synthetic membranes used in an engineered landfill to separate landfill contents from the environment. Compacted clay has also been used alone to provide a physical barrier and is still currently used today in conjunction with synthetic liners, to provide a secondary barrier. The potential of ENMs to penetrate or migrate through landfill liners is currently being studied; at this time, there is a lack of conclusive findings (Ganzleben et al., 2011). Academic bodies, such as the East Tennessee State University and the Environmental Research and Education Foundation (USA) are now undertaking this work.

Recent findings from Siddique (2013) suggest that properly designed and constructed landfills will be able to significantly limit nanoparticle transport to the environment for extended periods of time (approximately 100 years). In an experiment conducted by NanoHouse (Nanowaste Management), barrier properties of geomembranes were evaluated with suspensions of nanoparticles used in paints. It was found with this diffusion test that the nanoparticles did not cross the membrane, which corresponds to an effective efficiency of geomembranes over 12 years in real conditions (Zuin, 2013).

However, another study proposes that ENMs placed near the bottom of MSW landfills are of concern, as they may transport or diffuse through liners, especially if they are near the bottom of the landfill (Lozano and Berge, 2012). Since leachate, which is a mobile aqueous phase, could be released to the surrounding environment, human health risks could result (Boylard et al., 2013).

Synthetic membrane liners will likely contain ENMs and is currently being researched. However further research is needed, in particular to determine the potential risk of ENMs seeping through clay liners in older landfills or in situations where uncontrolled landfills depend on natural attenuation for treatment.

Nanomaterials and leachate treatment

Leachate treatment can incorporate one or a series of different systems such as aeration, sedimentation, settling lagoons, filtration, Ultra Violet (UV) treatment, and biological and/or chemical treatments. The purposes of these treatments are to settle out solids, adjust pH, increase oxygenation and break down or treat contaminants. The effectiveness of leachate treatment systems to adequately manage risks from ENMs will be influenced by the unique properties of ENMs and their behavior in landfill environments. Considerations include: 1) how ENMs interact with leachate and its potential to increase (or decrease) mobility and/or toxicity; 2) the integrity and nature of liners and their ability to contain ENMs and 3) the impact of ENMs on the effectiveness of the treatment technology itself.

Do current treatment technologies capture nanomaterials?

There is a lack of research specific to on-site landfill leachate treatment systems and their ability to contain and/or remove ENMs, although studies on the effectiveness of wastewater treatment technologies to remove ENMs have been reported. They are briefly mentioned here, to deduce the possible impact on landfill leachate treatment systems. Generally in studies of ENMs in wastewater treatment plants, nanoparticles bind with organic matter, which is ultimately settled out; some naturally aggregate with one another, thus improving settling; some bind with organic contaminants and some adhere to selective surfaces (DiSalvo et al., 2008).

Researchers have found that conventional wastewater treatment plants can effectively remove ENMs such as nano-silver oxide, nano-zinc oxide, nano-cerium oxide, nano-titanium dioxide (Ag°, ZnO, CeO_2 and TiO_2) from wastewater; however, the ENMs typically accumulate (> 90%) in the waste sludge or biosolids (Westerhoff et al., 2013). Additionally, with exception of nano-titanium dioxide (TiO_2), the initial mineralogy of silver, zinc and cerium (Ag, Zn and Ce) is transformed by oxidation, reduction and dissolution. This results in a transformation of the ENMs, whereby they do not exhibit the same properties as pristine ENMs (Bottero et al., 2015). Kaegi et al. (2011) found that nano-silver sorbs to wastewater biosolids and to a large extent and undergoes chemical transformation into silver sulfide (Ag_2S) which exhibits a much lower toxicity than other forms of silver (Ag). Kaegi et al. (2011) also indicated that further research is required to assess if other types of surface-coatings on ENMs may stabilise nano-silver or other ENMs in wastewater. Results from Nguyen M.D. (2013) indicated that nano-zinc oxide (ZnO) and nano-cerium oxide (CeO_2) impacted anaerobic digestion by inhibiting biogas production and found that the toxicity of the ENMs remained in biosolids, which could inhibit bacterial viability, seed germination and root growth of plants. However, Barton et al., 2014 recently studied the affinity of ENMs for sludge bacteria flocs using an experimental approach. The initial ENMs were transformed into new materials such as Ce-oxalate or silver sulfide (Ag_2S) or zinc monohydrogen phosphate (ZnHPO4), which would not have the same biological activity as the initial ENMs (Barton et al., 2014).

It is difficult to directly relate the efficiencies of ENM removal in wastewater treatment plants to landfill leachate, as leachate is primarily an aqueous effluent. However, it is suspected that ENMs would also bind to organic matter and bacteria in leachate. ENMs may be present in residual sludge as a result of the accumulation of settled solids during biological leachate treatment. Recent research has indicated the successful removal and sequestration of ENMs in biosolids and, in some cases, their transformation. However, ENMs remaining in the sludge could result in potential releases to the environment if the sludge is land applied or is sent to a landfill (DiSalvo et al., 2008, Lui et al., 2014, Westerhoff et al., 2013). Identifying the risk biosolids (containing ENMs) may pose is necessary to determine the appropriate management of the biosolids (further treatment as a waste or disposal). This requires consideration and further research; particularly the impact of disposing of biosolids containing ENMs in landfills.

What Best Available Technology is able to treat nanomaterials?

Best available technology treatment (BAT) technologies for ENMs have yet to be identified for on-site landfill treatment however, potential technologies are emerging. Although not all ENMs are toxic nor would they all require specialised treatment, it is necessary to prevent the release of ENMs deemed hazardous. This would begin by identifying optimal treatment by classifying these ENMs by hazard class, on a case-by-case basis. An approach to the treatment of nanowaste requires understanding of all its properties- not only chemical, but also physical and biological (Bystrzejewska-Piotrowska et al., 2009). Approaches to disposing of ENMs have been proposed and treatment systems for industrial effluents containing ENMs are also currently being studied. This may provide some useful information on technologies that could be effectively applied, adapted or combined with on-site landfill treatment systems.

A recent ANR (Agence Nationale de la Recherche) project NANOSEP (France) has shown that treatment technologies such as coagulation-flocculation, membrane filtration and flotation are very efficient in removing ENMs. This project has shown that the combination of flocculation and membrane separation to be very efficient. Lui et al. (2014) also identified and evaluated several treatment technologies that showed variations of success in removing ENMs in wastewaters including: 1) Coagulation and Electrocoagulation (EC) Process; 2) Flotation process; 3) Filtration process; 4) Biological process, and 5) other processes for ENM separation. Lui et al. (2014) also states that it may be difficult for one type of method to treat the complex matrix containing ENMs and different techniques are usually required in conjunction with one another to achieve better removal efficiency. Westerhoff et al. (2013) discuss the findings and effectiveness of 1) Separation of nanomaterials using membranes; 2) Biological transformation of nanomaterials during biological treatment and 3) the Removal of nanomaterials across continuous-flow wastewater treatment systems. DiSalvo et al. (2008) suggest, the removal of nanoparticles in aqueous streams (or effluents), such as leachate, could be accomplished with nanofiltration or reverse osmosis.

The European NANOFLOC project is currently looking at the development of new technology based on nano-suspension destabilisation and agglomeration of charged nanoparticles using electroflocculation. NANOFLOC is also exploring other possible methods including coagulation and sedimentation, flotation, magnetic separation (only for magnetic particles) or zero valent iron applications. None of these individual options are universally applicable or effective on their own at this time.

For the treatment of hazardous solid nanowastes to be effective, they should either be effective in strongly binding the ENMs in a solid matrix, or firmly securing them in a rigid impermeable container (Harford et al., 2007). Other methods such as vitrification for immobilising highly hazardous wastes, have been extensively studied for nuclear and industrial waste forms (Kavouras et al., 2003) and such an approach could be explored for highly hazardous nanowaste (Allan et al., 2009). Bystrzejewska-Piotrowska et al. (2009) suggest nanoparticle-containing waste should be stored in a way that prevents interaction of nanoparticles with water (possibly to diminish mobility). In the case of existing nanoparticle contamination in soil or water, novel bio-remediation techniques are also emerging, such as the use of mycoextraction (using fungi for the removal of contaminants) (Jakubiak et al., 2014).

Best available technologies, can be effective if accompanied by best management practices such as hazard classification, labelling and segregation for the appropriate end-of-life disposal management of ENMs deemed hazardous. For the treatment of ENMs in an aqueous phase, such as leachate (which may contain non-hazardous and hazardous ENMs) a suite of technologies show potential to effectively remove ENMs in wastewaters. Approaches currently being tested for industrial (or other) purposes may be applicable to the waste sector, although may require a combination of advanced treatment systems to remove ENMs from leachate.

Regulations and management of nanomaterials in waste

In 2013 the OECD adopted a recommendation on the safety testing and assessment of manufactured nanomaterials (OECD, 2013). This recognises “that the approaches for the testing and assessment of traditional chemicals are in general appropriate for assessing the safety of nanomaterials, but may have to be adapted to the specificities of nanomaterials" (OECD, 2013). Hence, regulations such as the European REACH legislation may be adequate in addressing the potential hazards of ENMs in many cases, especially once adapted to nanomaterials. Similarly, Breggin and Pendergrass (2007) have suggested that existing US regulations can cover ENMs. However, the literature also suggests that for some ENMs the current system of expressing toxicity may find limited application, requiring adjustments to existing control regimes and approaches for waste management. To date, the focus of environmental legislation and regulations has been on macroscale chemicals whereby risk is a function of exposure and hazard or toxicity as expressed in the form of mass per volume. Studies have suggested that the toxicity of some ENMs is a function of shape, size, surface reactivity and surface area (Breggin and Pendergrass, 2007; Musee, 2011; RCEP, 2008).

Knowledge gaps may limit the effective application of existing regulatory management controls. Key gaps include a lack of ENM hazard characterisation, understanding ENM behavior in landfill environments and knowledge of quantitative data on toxicity. For example, it is possible that manufacturing waste by-products in the nanoscale size range could require more stringent disposal requirements than for the parent products. There are risks that toxic by-products generated during nanotechnology manufacturing may be handled inadequately due to insufficient quantitative toxicity data, lack of transmission of information or available appropriate treatment techniques (Musee, 2011). It is important that certain ENMs are recognised as hazardous materials and the labelling or tagging of such nanoproducts be introduced to facilitate their separation and appropriate recovery in order to prevent them from entering municipal landfills (Bystrzejewska-Piotrowska et al., 2009). However, there is need for an official definition and appropriate classification regime of nanomaterials if product labelling is to be effective.

For consumer nanoproducts that may exhibit hazards upon disposal, labelling (or product information inserts) and proper disposal options could assist the appropriate management of these end-of-life products. Common consumer nanoproducts requiring special disposal could then be managed similarly to other household hazardous wastes. A nanoproduct, such as sunscreen, may not present a risk to the consumer, but may present varying hazards upon disposal (Musee, 2011) due to potential degradation of the product or potential interactions with other materials in the waste stream or the landfill environment. This is an area that requires further research and consideration.

Without knowing how companies plan to use and store recycled and non-recyclable ENMs, development of appropriate controls, regulations or other waste management protocols may be challenging. In order to adequately assess the potential risk posed by the use of ENMs, companies could be required to provide basic information on the quantities and characteristics of ENMs produced, used and discarded as well as estimated life-expectancy of the products containing nanoparticles (Powell et al., 2008). Although, generators of nanowastes may have insufficient information to provide to owners or operators of treatment, storage and disposal facilities to enable them to manage such wastes appropriately (Breggin and Pendergrass, 2007).

To reduce the potential risk of releases of ENMs to the environment from landfills, a combination of improvement in segregation and recovery/recycling efforts, adequate landfill design and operation, effective leachate treatment technologies and access to specialised facilities when required may be necessary. Identification, classification and labelling will support the implementation of improved and appropriate waste management approaches and the application of appropriate technologies to manage potential risks posed by certain ENMs. Adapting and clarifying existing legislative frameworks and current waste management approaches may be needed to restrict the flow of hazardous ENMs entering municipal waste landfills.

Conclusions and knowledge gaps

It is recognised that scientific knowledge of ENMs, their fate and behaviour in landfills is progressing and needs to be understood further to guide effective waste management approaches for the varied waste streams containing nanomaterials. However, recent research in this area raises complex issues to consider. There is evidence that some ENMs are released in landfill environments from products containing nanomaterials and from other nanowaste sources. Therefore it can reasonably be asserted that landfills currently contain ENMs and can be a pathway into the environment if ENMs are able to cross landfill liners (particularly from uncontrolled landfills) and pass through leachate treatment. Secondary pathways to be investigated include migration via landfill gases.

Landfills will increasingly receive greater amounts of ENMs over time, in conjunction with the growth of the nanotechnology industry and the broad use of these materials. The release of ENMs from products is likely under typical landfill conditions, particularly from liquid wastes containing ENMs or other waste products containing freely suspended nanoparticles. Landfills are unique and complex environments and ENM behaviour and their potential release is influenced by pH, anaerobic conditions, leachate composition and many other factors. For example, organic matter in leachate may enhance the mobility of ENMs, by preventing aggregation and precipitation. Physical stressors such as abrasion and compaction, may also aid in the release of ENMs in landfills.

ENMs are unlike any other known contaminant due to their unique physicochemical properties and characteristics such as size, shape, surface area and chemical reactivity. Nanowaste streams of different forms will vary from benign to extremely hazardous. Due to the binding and adsorptive properties of some ENMs, they may also enhance the toxicity and mobility of other pollutants. These unique properties could be highly problematic when combined with landfill leachate. In a worst case scenario, leachate, which already contains a variety of pollutants, may become more toxic, more bioavailable and mobilise other pollutants beyond landfills transporting them to distant ecosystems. However, ENMs may undergo transformations in landfills and the environment where they may no longer retain their original characteristics. These transformations will in turn affect the transport, fate and toxicity of ENMs in the environment.

The anti-microbial effects of ENMs in landfills have not been well researched; however ENMs could compromise the effectiveness of leachate treatment at high concentrations, where bacterial populations are used to break down pollutants. It is inconclusive as to whether ENMs can penetrate landfill liners, although this topic is currently being researched. The major concern remains with ENMs in collected leachate, when it leaves the landfill to be treated by wastewater treatment processes or is released directly to the environment with or without on-site treatment.

Although no specific information was found on best available technologies to remove ENMs in landfill leachate treatments systems, there are technologies used or being studied in industrial applications demonstrating various levels of success in removing certain

ENMs in wastewaters that could potentially be adapted to leachate treatment technologies, where necessary.

The unique properties of ENMs may challenge the ability of existing management systems and regulations to adequately identify and address ENMs; specifically the variable risks they may pose which differ from their bulk forms. ENMs may be handled under existing regulations; however clarification and adaptions may be required to adequately provide clear guidance to industry and regulators to avoid significant long-term liabilities for the public, businesses, insurers and investors.

Summary of knowledge gaps and areas of further research

While recent scientific knowledge has shed some light on the issue of ENMs in landfills, further research in the following areas is needed to improve our understanding of the problem and develop practical solutions:

a) *Development of analytical chemistry test methods to identify ENMs in environmental media, and distinguish them from normal scale chemicals they may contain.*

b) *Characterisation and quantification of the issue and understanding of the chemical and environmental processes in landfills:*

  i) Identify the types and quantities of ENMs and their individual level of hazard and potential exposure to evaluate the risk of products containing ENMs upon disposal and in nanowastes.

  ii) Identify and apply modern analytical methods available in other matrices (e.g. water, wastewater, gas) and investigate their applicability in studying ENM concentrations in leachate and landfill gas, as well as ENM fate and transport in landfills.

  iii) Understand the synergistic impacts of ENMs and typical contaminants in landfill leachate; specifically looking at key contaminants in leachate and studying the impact of ENMs on toxicity, bioavailability and transport of these contaminants.

  iv) Understand the process of ENM degradation and transformation in a landfill environment (in leachate) and the impact of degradation products; impact or release of ENMs from nanoproducts and nanowastes.

  v) Determine if there are ENM releases to air at the landfill surface or through landfill gas.

c) *Understanding the effectiveness and constraints of current landfill methods and technologies:*

  i) Understand the impacts of microbial properties of ENMs on on-site landfill treatment systems and other potential impacts that ENMs may have on leachate treatment systems.

  ii) Identify what key ENMs cross landfill liners and pass through leachate treatment systems and determine to what degree they are "treated" (similar to studies of ENMs in Waste Water Treatment Plants) by conventional methods or other technologies.

  iii) Determine the applicability of current BAT technologies, used in other wastewater treatment applications, to treat or remove ENMs in landfill leachate.

  iv) Develop effective methods of diverting hazardous ENMs from municipal landfills and treating waste containing hazardous ENMs (i.e. adequately handling residual waste containing ENMs such as biosolids or ash and not simply transferring them to landfills).

d) *Understanding the applicability of a future ENM classification system for waste management:*

   i) Examine the potential usefulness of classifying, labelling and segregating hazardous nanowastes and wastes containing hazardous ENMs, to effectively manage disposal through specialised hazardous waste landfills (or other treatment processes) as appropriate, to ensure adequate and safe disposal.

Notes

1. Macroscale chemicals are those refered to in traditional chemistry where observations can be made by the human eye. Contrarily, microscale or nanoscale objects are in the range of several micrometers (µm) or several nanometers (nm) respectively in size where observations cannot be made by the unaided eye and require the use of magnification devices such as optical microscopes or powerful microscopes such as the electron microscope or the scanning tunneling microscope. Microscale is around the size of a single living cell whereas nanoscale are about the size of single atoms or molecules, *www.cengage.com/resource_uploads/downloads/1439049300_222029.pdf*, *http://chem.sci.utsunomiya-u.ac.jp/v10n2/MashitaA/MashitaA_body.html.*
2. The NanoRelease project is anticipated to proceed in 4 phases, with the output of each phase determining scope and resources for subsequent phases. The first phase of the project consists mainly of a workshop sponsored/supported by the following organisations: US Environmental Protection Agency, Office of Research and Development, Environment Canada, Emerging Priorities Division, Health Canada, New Substances Assessment and Control Bureau, American Chemistry Council, Nanotechnology Panel, Society of Chemical Manufacturers and Affiliates, National Institute of Standards and Technology, The Adhesive and Sealant Council, American Cleaning Institute.
3. FRINano Project: A project that establishes a hands-on measurement technique for the quantification and characterisation of pigment nanoparticles, which might be released from coatings or plastics upon weathering and/or exposure to mechanical stress. See: *www.vdmi.de/englisch/topics/nano.html.*
4. CarboSafe Project: An alliance initiative that develops reliable measuring technologies for unambiguously determining the release rates of nanoparticles in the lifecycle of CNT-based products. Furthermore, the project aims to identify the ecotoxicological potential of carbon nanotubes and to accurately estimate the risk potential with the aid of newly developed measuring technologies. See: *www.nanopartikel.info/en/projects/completed-projects/innocnt-carbosafe.*
5. CarboLifeCycle Project: A research project on nano-safety aspects with an enphasis on ecotoxicological consideration and development of measurement engineering, the advancement of measurement strategies and the measurement of potential exposure within the production, processing, utilisation and "end of life" of CNT's or CNT containing products. See: *www.nanopartikel.info/en/projects/completed-projects/carbolifecycle.*

References

Allan, J. et al. (2009), *Comparison of Methods Used to Treat Nanowaste from Research and Manufacturing Facilities*, University of Western Sydney & University of Queensland.

Asmatulu, E. et al. (2012), "Life cycle and nano-products: end-of-life assessment", *Journal of Nanoparticle Research*, Vol. 14, pp. 720.

Auffan, M. et al. (2012), "Is There a Trojan-Horse Effect during Magnetic Nanoparticles and Metalloid Cocontamination of Human Dermal Fibroblasts?", *Environmental Science and Technology*, Vol. 46, No. 19, pp. 10789-10796.

Barton, L.E. (2014), "Theory and Methodology for determining Nanoparticle Affinity for Heteroaggregation in Environmental Matrices Using Batch Measurements", *Environmental Engineering Science*, Vol. 31, No. 7, pp. 421-427.

Baun, A. et al. (2008), "Toxicity and bioaccumulation of xenobiotic organic compounds in the presence of aqueous suspensions of aggregates of nano-C60", *Aquatic Toxicology*, Vol. 86, No. 3, pp. 379-387.

Boldrin, A. et al. (2014), "Environmental exposure assessment framework for nanoparticles in solid waste", *Journal of Nanoparticle Research*, Vol. 16, No. 6, pp. 2394.

Bolyard, S. (2011), *Fate of Nanomaterials in Municipal Solid Waste Landfills*, *https://nees.org/resources/2105*.

Bolyard, S. et al. (2012), *The Fate and Transport of Nanoparticles in Municipal Solid Waste Landfills*, University of Central Florida, *http://pure.ltu.se/portal/files/36938608/TR.Anders_Lagerkvist.Komplett.pdf*.

Botta et al. (2011), "TiO_2-based nanoparticles released in water from commercialised sunscreens in a life-cycle perspective: structures and quantities", *Environmental Pollution*, Vol. *159, No.* 6, pp. 1543-1550.

Bottero, J.Y. et al. (2015), "Nanotechnology, Global Development in the frame of Risk Forecasting, A necessity of interdisciplinary researches", *Comptes Rendus Géoscience*, Vol. 347, No. 1, pp. 35-42.

Breggin, L.K. and J. Pendergrass (2007), *Where Does the Nano Go? End-of-Life Regulation of Nanotechnologies*, Woodrow Wilson International Center for Scholars, Project on Emerging Nanotechnologies, PEN 10.

BSI (2007), *Nanotechnologies-Part 2: Guide to safe handling and disposal of manufactured nanomaterials*, British Standards, PD 6699-2:2007.

Bystrzejewska-Piotrowska, G. et al. (2009), "Nanoparticles: Their potential toxicity, waste and environmental management", *Waste Management*, Vol. 29, No. 9. pp. 2587-2595.

Cheng, X. et al. (2004), "Naphthalene adsorption and desorption from aqueous C-60 fullerene", *Journal of Chemical Engineering and Data*, Vol. 2004, No. 49, pp. 675-83.

Conestoga-Rovers & Associates (2013), *Landfill Monitoring Data- Correlation, Trends, and Perspectives*, for Environment Canada.

DiSalvo, R. et al. (2008), *Evaluating the Impact of Nanoparticles on Wastewater Collection and Treatment Systems in Virginia*, Draper Aden Associates Inc.

Edouk, S. et al. (2013), "Evaluation of Engineered nanoparticle toxic effect on wastewater microorganisms: Current status and challenges", *Ecotoxicology and Environmental Safety*, Vol. 95, No. 2013, pp. 1-9.

Eggen, T. et al. (2010), "Municipal landfill leachates: A significant source for new and emerging pollutants", *Science of the Total Environment*, Vol. 408, No. 21, pp. 5147-5157, *http://dx.doi.org/10.1016/j.scitotenv.2010.07.049*.

Farré, M. et al. (2009), "Ecotoxicity and analysis of nanomaterials in the aquatic environment", *Analytical and Bioanalytical Chemistry*, Vol. 393, No. 1, pp. 81-95".

Ganzleben, C. et al. (2011), "Review of Environmental Legislation for the Regulatory Control of Nanomaterials", Milieu Ltd. and AMEC Environment & Infrastructure UK Ltd., *http://ec.europa.eu/environment/chemicals/nanotech/pdf/review_legislation.pdf*.

Gao, J. et al. (2008), "Nanowastes and the Environment: Using Mercury as an Example Pollutant to Assess the Environmental Fate of Chemicals Adsorbed onto Manufactured Nanomaterials", *Environmental Toxicology and Chemistry*, Vol.27, No. 4, pp. 808-810.

Gomez-Rivera, F. (2011), "Exploration of Biological Treatment Systems for the Removal of Persistent Landfill Leachate Contaminants and Nanoparticles", Dissertation-University of Arizona.

Hansen, S.F. et al. (2008), "Categorization framework to aid exposure assessment of nanomaterials in consumer products", *Ecotoxicology*, Vol. 17, No. 5, pp. 438-47 *http://link.springer.com/article/10.1007%2Fs10646-008-0210-4*.

Hansen, S.F. (2009), "Regulation and Risk Assessment of Nanomaterials: too little too late?", PhD Dissertation, Department of Environmental Engineering, Technical University of Denmark.

Harford et al. (2007), "Current OHS best practices for the Australian nanotechnology industry", *position paper*, the NanoSafe Australia Network.

He, F. et al. (2012), "Rapid Removal of Hg(II) from Aqueous Solutions Using Thiol-Functionalized Zn-Doped Biomagnetite Particles", *ACS Applied Materials and Interfaces*, Vol. 4, pp. 4373-4379.

Health Council of the Netherlands (2011), *Nanomaterials in Waste*, The Hague: Health Council of the Netherlands, publication no. 2011/14E, *www.gezondheidsraad.nl/sites/default/files/Nano_waste_201114E.pdf*.

Hennebert, P. et al. (2013), "Experimental evidence of colloids and nanaoparticles presence from 25 waste leachates", *Waste Management*, Vol. 33, No. 9, pp. 1870-1881.

Holden, P. et al. (2014), "Five reasons to use bacteria when assessing manufactured nanomaterial environmental hazards and fates", *Current Opinion in Biotechnology*, Vol. 27, pp. 73-78.

Hou, L et al. (2012), “Removal of silver nanoparticles in simulated wastewater treatment processes and its impact on COD and NH4 reduction”, *Chemosphere*, Vol. 87, No. 3, pp. 248-252.

Hyung, H. and J.H. Kim (2008), “Natural organic matter (NOM) adsorption to multiwalled carbon nanotubes: Effect of NOM characteristics and water quality parameters”, *Environmental Science and Technology*, Vol. 42, No. 12, pp. 4416-4421.

ILSI (n.d.) “NanoRelease Project”, International Life Sciences Institute, *www.ilsi.org/ResearchFoundation/RSIA/Pages/NanoRelease1.aspx*.

Jaisi, D.P. et al. (2008), “Transport of single-walled carbon nanotubes in porous media: filtration mechanisms and reversibility”, *Environmental Science and Technology*, Vol. 42, No. 22, pp. 8317-8323.

Jakubiak, M. et al. (2014), “Bioaccumulation and biosorption of inorganic nanoparticles: factores affecting the efficiency of nanoparticle mycoextraction by liquid-grown mycelia of *Pleurotus enyngii* and *Tramete versicolor*”, *Mycological Progress*, Vol. 13, No. 13, pp. 525-532.

Kaegi, R. et al. (2011), “Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant”, *Environmental Science and Technology*, Vol. 45, No. 9, pp. 3902-3908.

Kavouras, P. et al. (2003), “Microstructural changes of processed vitrified solid waste products”, *Journal of European Ceramic Society*, Vol. 23, No. 8, pp. 1305-11.

Keller, A.A. et al. (2013), “Global life cycle releases of engineered nanomaterials”, *Journal of Nanoparticle Research*, Vol. 15 No. 6.

Kim, Y. (2014), “Nanowastes treatment in environmental media”, *Environmental Health and Toxicology*, Vol. 29, pp. 2233-6567.

Klaine, S.J. et al. (2008), “Nanomaterials in the environment: behaviour, fate, bioavailability, and effects”, *Environmental Toxicology and Chemistry*, Vol. 27, No. 9, pp. 1825-51.

Kurniawan, T.A. et al. (2006), “Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate”, *Journal of Hazardous Materials*, Vol. 129, No. 1-3, pp. 80-100.

Labille J. et al. (2010), “Aging of TiO2 nanocomposites used in sunscreen. Dispersion and fate of the degradation products in aqueous environment”, *Environmental Pollution*, Vol. 158, No. 12, pp. 3482-3489.

Lecoanet, H.F. et al. (2004), “Laboratory assessment of the mobility of nanomaterials in porous media”, *Environmental Science and Technology*, Vol. 38, No. 19, pp. 5164-5169.

Leppard, G.G. et al. (2004), “Electron-optical characterization of nano- and micro-particles in raw and treated waters: an overview”, *Water Science and Technology*, Vol. 50, No. 12, pp. 1-8.

Limbach, L.K. et al. (2007), “Exposure of Engineered Nanoparticles to Human Lung Epithelial Cells: Influence of Chemical Composition and Catalytic Activity on Oxidative Stress”, *Environmental Science and Technology*, Vol. 41, No. 11, pp. 4158-4163.

Lin, D. and B. Xing (2008), “Tannic acid adsorption and its role for stabilising carbon nanotube suspensions”, *Environmental Science and Technology*, Vol. 42, No. 16, pp. 5917-5923.

Lin, D. et al. (2010), “Fate and Transport of Engineered Nanomaterials in the Environment”, *Journal of Environmental Quality*, Vol. 39, No. 6, pp. 1896-908.

Lozano, P. and N.D. Berge (2012), “Single-walled carbon nanotube behaviour in representative mature leachate”, *Waste Management*, Vol. 32, No. 9, pp. 1699-1711.

Lowry, G.V. et al. (2012), “Transformations of Nanomaterials in the Environment”, *Environmental Science and Technology*, Vol. 46, No. 13, 6893-6899.

Lui, Y. et al. (2014), “Nanoparticles in wastewaters: Hazards, fate and remediation”, *Powder Technology*, Vol. 255, pp. 149-156.

Marcoux, M.A. et al. (2013), “Review and prospect of emerging contaminants in waste – Key issues and challenges linked to their presence in waste treatment schemes: General aspects and focus on nanoparticles”, *Waste Management*, Vol. 33, No. 11, pp. 2147-2156.

Maurer-Jones, M.A. et al. (2013), “Toxicity of Engineered Nanoparticles in the Environment”, *Analytical Chemistry*, Vol. 85, No. 6, pp. 3036-3049.

Mueller, N.C. and B. Nowack, (2008), “Exposure Modeling of Engineered Nanoparticles in the Environment”, *Environmental Science and Technology*, Vol. 42, No. 12, pp. 4447-4453.

Mueller, N.C. et al. (2012), "Nanomaterials in waste incineration and landfill", Internal Empa-report, *www.empa.ch/plugin/template/empa/*/124595*.

Musee, N. (2011), "Nanowastes and the Environment: Potential New Waste Management Paradigm", *Environment International*, Vol. 37, No. 1, pp. 112-128.

Musee, N. (2010), "Nanotechnology risk assessment from a waste management perspective: Are the current tools adequate?" *Human and Experimental Toxicology*, Vol. 30, No. 8, pp. 820-835.

Nguyen, M.D. (2013), *Effects of CeO2 and ZnO nanoparticles on Anaerobic Digestion and Toxicity of Digested Sludge*, Dissertation, University of Dalat, Viet Nam.

Nowack, B. et al. (2013), "Potential release scenarios for carbon nanotubes used in composites", *Environment International*, Vol. 59, pp. 1-11.

OECD (2013), "Recommendation of the Council on the Safety Testing and Assessment of Manufactured Nanomaterials", *http://acts.oecd.org/Instruments/ShowInstrumentView.aspx?InstrumentID=298&InstrumentPID=314&Lang=en&Book=False*.

Pal, S. et al. (2007), "Does the antibacterial activity of silver nanoparticles depend on the shape of the nanoparticle? A study of the gram-negative bacterium Escherichia coli", *Applied and Environmental Microbiology*, Vol. 73, No. 6, pp. 1712-20.

Petosa, A.R. et al. (2010), "Aggregation and deposition of engineered nanomaterials in aquatic environments: role of physicochemical interactions", *Environmental Science and Technology*, Vol. 44, No. 17, pp. 6532-6549.

Powell, M.C. et al. (2008), "Bottom-up risk regulation? How nanotechnology risk knowledge gaps challenge federal and state environmental agencies", *Environmental Management*, Vol. 42, No. 3, pp. 426-443.

Project on Emerging Nanotechnologies (2014), "Consumer Inventory", *www.nanotechproject.org/cpi* and *www.nanotechproject.org/cpi/about/analysis* (accessed May 2014).

Project NANOFLOC (n.d.) "Electro-agglomeration and separation of Engineered NanoParticles from process and waste water in the coating industry to minimise health and environmental risks", *www.asio.cz/en/nanofloc*.

Reinhart, D.R. et al. (2010), "Emerging contaminants: nanomaterial fate in landfills", *Waste Management*, Vol. 30, No. 11, pp. 2020-2021.

Royal Commission on Environmental Pollution (2008), *Novel Materials in the Environment: The case of nanotechnology*, 27th report, *www.gov.uk/government/uploads/system/uploads/attachment_data/file/228871/7468.pdf*.

Saleh, N.B. et al. (2010), "Influence of biomacromolecules and humic acid on the aggregation kinetics of single-walled carbon nanotubes", *Environmental Science and Technology*, Vol. 44, No. 7, pp. 2412-2418.

Siddique, S.N. (2013), "Simulation of Fate of Nanoparticles in Landfill Barrier Systems", Dissertation-University of Western Ontario (Canada).

Templeton, R.C. et al. (2006), "Life-cycle effects of single-walled carbon nanotubes (SWNTs) on an estuarine meiobenthic copepod", *Environmental Science and Technology*, Vol. 40, No. 23, pp. 7387-7393.

US EPA (2014), "Technical Factsheet- Nanomaterials", United States Environmental Protection Agency, January 2014, *www2.epa.gov/sites/production/files/2014-03/documents/ffrrofactsheet_emergingcontaminant_nanomaterials_jan2014_final.pdf*.

von der Kammer, F. et al. (2014), "Spot the Difference: Engineered and Natural Nanoparticles in the Environment–Release, Behavior, and Fate", *Angewandte Chemie International Edition, Special Issue: Nanotechnology & Nanomaterials, Nanotoxicology & Nanomedicine*, Vol. 53, No. 46, pp. 12398-12419.

Walser, T. et al. (2012), "Persistence of Engineered Nanoparticles in a Municipal Solid Waste Incineration Plant", *Nature Nanotechnology*, Vol. 7, pp. 520-524.

Westerhoff, P. et al. (2013), "Nanomaterial Removal and Transformation during Biological Wastewater Treatment", *Environmental Engineering Science*, Vol. 30, No. 3, pp. 109-120.

Westerhoff, P. et al. (2008), "Properties of commercial nanoparticles that affect their removal during water treatment", in Grassian V. H. (ed), *Nanoscience and Nanotechnology: Environmental and Health Impacts*, John Wiley and Sons; 2008. p. 71-90.

WSP Canada (2014), *Effectiveness of Conventional and Advanced in Situ Leachate Treatment*, (for Environment Canada).

Yang, Y et al. (2013), “Nanosilver impact on methanogenesis and biogas production from municipal solid waste”, *Waste Management*, Vol. 32, No. 5, pp. 816-825.

Yang, Y. et al. (2006), “Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials”, *Environmental Science and Technology,* Vol. 40, No. 6, pp.1855-1861.

Zhang, Y. et al. (2008), “Stability of commercial metal oxide nanoparticles in water”, Water Research, Vol. 42, pp. 2204-2212.

Zuin, S. et al. (2013) “‘Nanowaste’ Management”, NanoHouse Dissemination report, No. 2013-05, *www-nanohouse.cea.fr/home/liblocal/docs/Dissemination%20Reports/NanoHouse%20DR5.pdf*.

Nanomaterials in Waste Streams
Current Knowledge on Risks and Impacts

Chapter 5

The fate of engineered nanomaterials in sewage treatment plants and agricultural applications

This chapter investigates the current state of knowledge on engineered nanomaterials (ENMs) and their behaviour in wastewater treatment processes in order to identify areas for future research. It focuses on the processes currently in use for urban sewerage treatment and begins by investigating the presence of engineered nanomaterials in wastewater treatment plants. It the moves on to examine the possible retention and aggregation of engineered nanomaterials in activated sludge and explores the possible transformations that ENMs can undergo in treatment plants and the models that are available to predict these transformations. The chapter also discusses the potential risks of agricultural application of sewerage sludge that is charged with engineered nanomaterials. The chapter concludes by identifying knowledge gaps and areas where additional research would be required.

This report investigates the current state of knowledge on engineered nanomaterials (ENMs) and their behaviour in wastewater treatment processes in order to identify areas for future research.

This chapter first covers the general processes of wastewater treatment and investigates the presence of engineered nanomaterials in wastewater treatment plants. It then examines the possible retention and aggregation of engineered nanomaterials in activated sludge and explores the use of retention, aggregation and sedimentation models. The chapter also looks into the possible impacts of engineered nanomaterials accumulated in sewage sludge bound for agricultural applications. It also identifies current international research around this area. Finally, the chapter highlights knowledge gaps and areas where additional research would be required.

Processes used in urban sewage treatment plants: the role of activated sludge

Sewage treatment plants collect wastewater from urban and/or industrial sources. Urban wastewater arises from human activities (toilets, showers, dish-washing, etc.). The amount of sludge produced is hard to gauge. However, a 2004 report by ADEME (French Environment and Energy Management Agency) confirmed this fact. The produced figures show that, agricultural applications represent significant quantities (Table 5.1).

Table 5.1. **Production and management of sewage treatment plant sludge in France (2000-04)**

			Agricultural recovery
Dry material (tonne/year)	Urban Sludge	887 755	524 290
	Industrial Sludge	950 000	600 000
Raw material (tonne/year)	Urban Sludge	8×10^6 to 10×10^6	5×10^6 to 6×10^6
	Industrial Sludge	3.5×10^6 to 4×10^6	1.9×10^6 to $.3\times10^6$

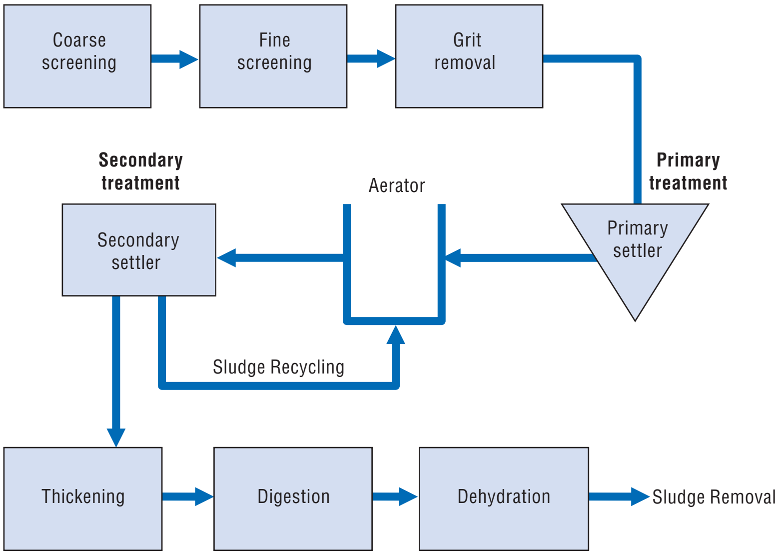
Source: ADEME, 2004.

Most plants are biological treatment plants. They are based on biological processes and are sometimes linked to physical/chemical processes (flocculation, chlorination, etc.). Figure 5.1 shows the stages in a process used in an urban sewage treatment plant.

The first stages are means of removing the largest objects: coarse + fine screening + grit removal.

The section which corresponds to biological treatment is carried out in an aerator (addition of air) followed by sedimentation of the sludge which is recycled to the top of the aeration reactor. The sludge which is not recycled is thickened, then digested (in an anaerobic reactor) which stabilises the organic matter (less odour) and reduces its toxicity (blocking metals and pathogens), breaks down organic carbon and reduces the mass (dry matter) of the sludge to be disposed; from 35 to 40% for dry matter – 40 to 50% for volatile matter.

Figure 5.1. **Wastewater treatment stages**



Source: From ADEME (2004): *www.ademe.fr*.

Biological treatment reduces organic pollution via heterotrophic bacteria which use the organic material as an energy source. The resulting bacterial development is also used to adsorb (absorb) metallic elements and to aggregate any particles which were not removed by the initial screening process.

Biological sewage treatment plants form the majority of liquid effluent treatment plants. This treatment is also known as activated sludge treatment, i.e. by using a collection of bacteria with the aim of breaking down organic contaminants (pesticides, medical residues, etc.), blocking metals and metalloids, and denitrifying effluents, etc. This is a complex process and also involves biochemical reactors and physical processes such as aggregation, sedimentation, etc. Activated sludge is a complex material (Schmid et al., 2003) made up of bacterial aggregates measuring ~500 µm, themselves formed from microaggregates measuring ~10 µm (Snidaro et al., 1997). The fractal structure with a dimension of approx. 2.2 micro meters limits the transfer of water to the core of the aggregate. The bacterial diversity within the aerobic reactor, for example, ensures that there is a wide range of reactivity.

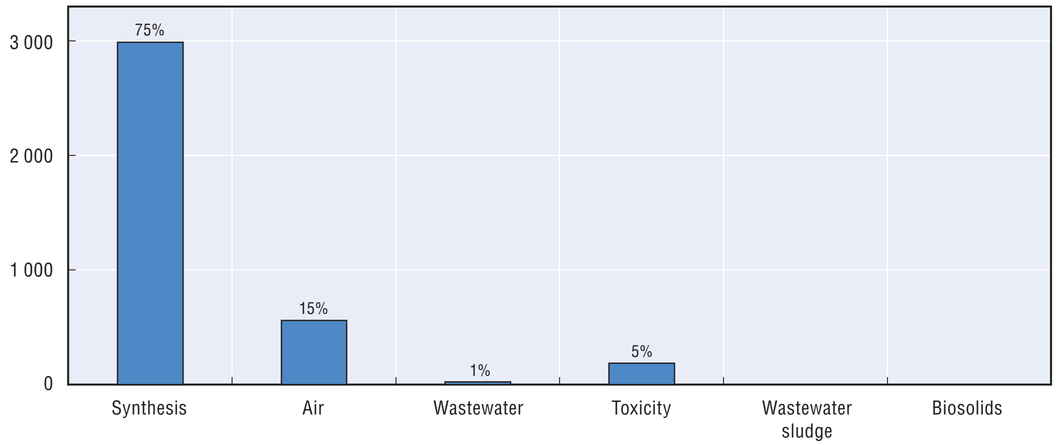
As well as bacteria there are polymers (proteins and polysaccharides) which also have a role to play in "capturing" the various contaminants.

What do we know about the presence of nanomaterials in the sludge from sewage treatment plants?

Although sewage treatment plants receive some wastewater containing metals and nanomaterials (Blaser et al., 2008), very few studies had examined detection of nanomaterials in biological sludge from sewage treatment plants as demonstrated by the exhaustive study carried out by Brar, S. K. et al. (2010) (Figure 5.2).

A study financed by the US EPA ("Targeted National Sewage Sludge Survey Statistical Analysis Report"– EPA-822-R-08-018 – April 2009) indicates the presence of significant concentrations of silver (Ag) or even titanium (Ti) in sludge from urban sewage treatment plants (Figure 5.3). A subsequent study on samples from the EPA's work shows the presence

Figure 5.2. **Publications on nanomaterials corresponding to certain research fields**



Source: Brar, S. K. et al. (2010).

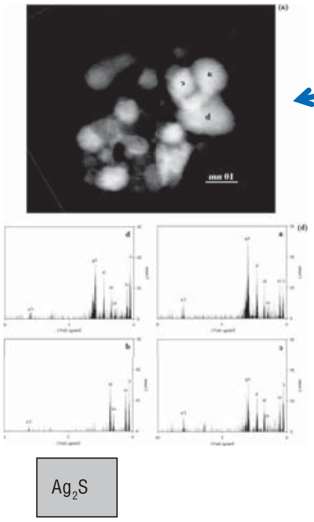
of nanoparticles of silver sulphide (Kim et al., 2010). These nanoparticles of silver sulphide result from oxidation of silver metal to form Ag^+ and precipitation of Ag^+ to form Ag_2S which is thermodynamically stable (Figure 5.3).

Figure 5.3. **Concentration of metallic elements and presence of Ag2S nanoparticles in urban sludge**

Understanding AgNps formation/transformation in wastewater treatment

EPA United States Environmental Protection Agency

Targeted National Sewage sludge Survey
Statistical Analysis Report
(Released in Jan 2009)



Sludge ID 68349 (from Midwest region)
Elemental Analysis

Element	($mg\ kg^{-1}$)
Ag	**856**
Al	57 300
Ca	98 900
Cu	**1 720**
Fe	**51 000**
Mg	13 500
Mn	**1 070**
Na	6 080
P	57 200
Ti	**4 510**
Zn	**1 530**

Source: US EPA (2009) and Kim et al. (2010).

Engineered Nanomaterials (ENMs) are bound to be present in sewage treatment plants given that they are to be found in everyday consumer products such as cosmetics, coatings, the agri-food sector, etc. (Brar et al., 2010) and that sewage treatment plants in OECD Member countries are the main channel for wastewater from human activities. In 2010 over 7 billion m^3 (domestic wastewater and rainwater) passed through sewage treatment plants. See Table 5.2 for details.

Table 5.2. **Occurrence of nanoparticles originating from everyday consumer products**

Source	Type of nanoparticle	Quantity used in terms of tonnes	Applications
Metals and alkaline earth metals	Ag	High	Antimicrobials, paints, coatings, medical use, food packaging
	Fe	High	Water treatment
	Pt	High	Catalysts
	Sn	Unknown	Paints
	Al	High	Metallic coating/plating
	Cu	Unknown	Microelectronics
	Zr	High	
	Se	Low	Nutraceuticals, health supplements
	Ca	Low	Nutraceuticals, health supplements
	Mg	Low	Nutraceuticals, health supplements
Metal oxides	TiO_2	High	Cosmetics, paints, coatings
	ZnO	Low	Cosmetics, paints, coatings
	CeO_2	High	Fuel catalyst, Paints
	SiO_2	High	Paints, coatings
	Al_2O_3	Low	Usually substrate bound, paintings
Carbon materials	Carbon black	High	Substrate bound, but released with tyre wear
	Carbon nanotubes	Medium-High	Used in a variety of composite materials
	Fullerenes (C_{60}-C_{80})	Medium-High	Medical and cosmetics use
Miscellaneous	Nanoclay	High	Plastic packaging
	Ceramic	High	Coatings
	Quantum dots	Low	Different compositions
	Organic nanoparticles	Low	Vitamins, medicines, carriers for medicines and cosmetics, food additives and ingredients

Source: Brar, S.K. et al. (2010).

What transformations can nanoparticles undergo in sewage treatment plants and how does this affect reactor operation?

Physico-chemical transformations of engineered nanomaterials (ENMs)

In the initial stages of sewage treatment plants, nanoparticles resulting from changes in the products containing such particles will experience aggregation, sedimentation in various compartments and also, in some cases, radical transformation which may affect their concentration in effluents, but also in the sludge which will go on to follow different routes such as incineration, storage or agricultural applications. It is therefore important to understand and predict the fate of these ENMs when treating wastewater from industrial or domestic sources. Cosmetics products, for example, include surface-functionalised ZnO and TiO_2 nanoparticles, which may be found in surface water after passing through a wastewater treatment plant (Kiser et al., 2009; Auffan et al., 2010a, 2010b; Westerhoff et al., 2011).

More recent studies on the effects and transformation of nanomaterials or nanoparticles in activated sludge from a sewage treatment plant were generally carried out in a controlled reactor or with a pilot plant in a laboratory. The most extensively studied nanomaterials include nanoparticles of silver metal, followed by ZnO, TiO_2, CeO_2, SiO_2 and carbon nanotubes.

Injected nanomaterials such as TiO_2, Ag°, CeO_2 or Cu are largely eliminated from wastewater through primary and secondary treatment (Kiser et al., 2009 and 2010; Kaegi et al., 2011; Ganesh et al., 2010; Wang et al., 2012; Gomez-Rivera et al., 2012). Nanoparticles are then associated with the solid phases of sludge by over 80% by mass. Mechanisms which lead to such associations include heteroaggregation between nanoparticles and bacteria, plus adsorption and interactions with biological polymers (Wang et al., 2012). Other authors have suggested that physicochemical transformations linked to interactions with living organisms play an important role (Tiede et al., 2010). It appears that the diversity of nanoparticles, their surface functionalisation within products, and their specific surface area etc., will affect their removal in terms of both kinetics and quantity (Kiser et al., 2009 and 2010; Jarvie et al., 2009; Tiede et al., 2010; Barton et al., 2013, 2014a, 2014b). The small proportion leaving the plant would remain in the form of nanoparticles and end up in surface water (Tiede et al., 2010; Kim et al., 2010).

Work on nanoparticles' stability in wastewater during the treatment process (Limbach et al., 2008) has shown that cerium oxide, CeO_2, has an affinity for proteins and in particular for peptides. The zeta potential was modified and increased the stability of the nanoparticles. A similar study with Ag° showed that nanoparticles were very stable and less effectively removed when surface functionalised (Kiser et al., 2010), whereas non-functionalised nanoparticles were associated with the solid phase.

It was demonstrated that nanoparticles associate quickly with the particles present in wastewater and then transformed in the case of Ag° via oxidation and sulfidation (Kaegi et al., 2011; Liu et al., 2011; Doolette et al., 2013; Ma et al., 2012). This sulfidation modifies reactivity insofar as it reduces solubility and toxic potential because Ag_2S is thermodynamically stable and not a biocide nanoparticle (Levard et al., 2011 and 2012). Similar data was obtained for nanoparticles of ZnO (Lombi et al., 2012) using a pilot wastewater treatment plant and compost to analyse the transformations within the sludge. The results show that ZnO is rapidly transformed to ZnS during effluent treatment. ZnS was dissolved in the compost and the Zn^{2+} ions are partially precipitated in the form of zinc phosphate and also combine with iron oxyhydroxides.

A recent study (Barton et al., 2013) conducted by using a laboratory reactor with activated sludge in aerobic mode with non-functionalised and functionalised industrial CeO_2 nanoparticles with citrate molecules and low added concentrations (~1mg/L after one month) showed that Ce(IV) had been reduced to form Ce(III) with precipitation of $Ce(III)PO_4$. The reduction kinetics of cerium IV differed for surface-functionalised and non-surface-functionalised CeO_2. The reaction worked faster in the case of non-functionalised CeO_2, reaching 30% within the bacterial aggregates, and ~12% in the case of CeO_2 that was coated with citrate after 24 hours. This shows that direct contact with the bacterial membranes plays an important role with regard to physicochemical transformations of metal oxide nanoparticles (Thill et al., 2006; Zeyons et al., 2010). The presence of surface functionalisation with organic or mineral molecules (Auffan et al., 2010a) reduces the transformation kinetics and toxicity. Surface functionalised nanoparticles can slow down transformation kinetics (e.g. oxidation, reduction) and negatively affect the wastewater treatment process. However, it could also be anticipated from this report that surface functionalised nanoparticles (if the coating is stable) reduce toxicity, which would be a positive effect. A summary is provided in Box 5.1 below.

Box 5.1. **Summary of physico-chemical transformations of engineered nanomaterials (ENMs)**

Chemical transformations in sewage treatment plants, such as solubilisation by reduction (e.g. CeO_2) or oxidation (e.g. Ag°), are important parameters to be taken into consideration in nanometric material balances. These chemical transformations are accompanied by precipitation in the form of mineral species such as Ag_2S or $CePO_4$ which are thermodynamically stable and seemingly less toxic than the original materials. Widespread surface functionalisation in order to introduce nanoparticles into common products may slow down these transformations and maintain the initial oxidation or reduction state for longer by limiting contact with bacterial aggregates.

Operation of the various process stages

Researchers have examined a number of effects:

- the change in dissolved oxygen demand
- nitrification and denitrification
- the impact on methanogenesis in the reactor in anaerobic mode and volatile organic acids during sludge composting
- biological oxygen demand
- bacterial diversity
- the decrease or change in the chemistry of extra-cellular polymers (proteins in particular)
- cell death
- mechanisms by which nanoparticles interact with bacteria
- the influence of sludge sedimentation as a function of changes in sludge structure.

The results do not point to consistent messages. For example:

- A paper on the impact of adding Ag° nanoparticles compared with adding silver salts (Ag+) (Arnaout and Gunsch, 2012) on the denitrification process shows that citrate-coated Ag° nanoparticles were associated with maximum denitrification inhibition at concentrations of ~2 ppm. This data completely contradicts the observations of Kiser et al., 2010. Other authors (Yang et al, 2013) noted that the effects on anaerobic digestion were negligible up to silver nanoparticle concentrations of 40 mg/L.
- Multi-walled carbon nanotubes were tested on samples of activated sludge in an aeration reactor in Massachussetts in order to assess the effects on respiration and the production of exocellular polymers. The authors demonstrate that inhibition is dependent on concentration, but for carbon nanotube concentrations > 0.64 g/L (Luongo et al, 2010).

- A critical review (Yang et al, 2013) of the impact of metallic nanoparticles on anaerobic digestion suggested low or zero effects with regard to bacterial diversity in the absence of oxygen in the case of TiO_2, Ag°, ZnO.
- This is partly contradicted by an article by Z. Liang et al.in 2010 concerning Ag°, which shows that the community of nitrifying bacteria decreases over time.

A summary is provided in Box 5.2 below.

Box 5.2. **Summary of operation of the various process stages**

Work on the operation of the various treatment stages (see Figure 5.1) is still in its early stages and requires a more systematic approach to the development of bacterial communities in aerobic and anaerobic reactors according to nanomaterials' doses and their surface formulation, insofar as these communities are the source of the above-mentioned reactions. Experiments involving high concentrations appear to be of limited credibility.

Can we predict the retention and transformation of ENMs by activated sludge? Use of retention, aggregation and sedimentation models

Current data shows that the majority of ENMs accumulate in biological aggregates in sewage treatment plants and these biological solids are then partly recycled in compost. We know that some nanoparticles such as ZnO, Ag°, CeO_2 are transformed and that the transformation kinetics (oxidoreduction + dissolution + precipitation, etc.) are dependent not only on the presence of surface functionalisation, but also on direct contact with biological membranes such as in the case of some biological species which display more active electron transfer behaviour. However, this does not apply in the case of one of the most common ENMs: TiO_2. TiO_2 is not particularly soluble and its photocatalytic activity, which generates powerful oxidising agents, is dependent on the size and extension of certain mineralogical faces (Auffan et al., 2009a, 2009b).

A recent paper by Barton et al., (2014a), written as part of a co-operation between CEINT in the USA, GDR I I-CEINT and Labex SERENADE in France, systematically measures the quantity of nanoparticles associated with biosolids in a pilot urban sewage treatment plant (aerobic and anaerobic reactor) in Durham (North Carolina), and shows that, for brief contact times:

- ~90% of CeO_2, ZnO and TiO_2 nanoparticles were combined with bacterial aggregates
- ~60% of Ag° nanoparticles were combined with bacterial aggregates

after just one hour of contact. See Table 5.3 for details.

Surface-functionalised and non-functionalised nanoparticles were observed to behave differently. At low concentrations (< 10 ppm), non-functionalised nanoparticles were retained to a greater extent in bacterial aggregates than functionalised nanoparticles. Similarly, the energy dissipated in reactors plays an important role in the likelihood of encountering objects and helps to increase the nanoparticles which combine with bacterial aggregates when the mixing energy increases.

Table 5.3. **Percentage of nanoparticles associated with bacterial aggregates in an aerobic and anaerobic reactor of an urban sewage treatment plant**

Sample	Description	Sludge Type	Percent Removal					
			1 ppm		10 ppm		50 ppm	
			Low mixing	High mixing	Low mixing	High mixing	Low mixing	High mixing
Ag 1	40nm Ag PVP	Primary			17	27	52	48
		Secondary			22	42	30	58
Ag 2	8nm Ag PVP	Primary			11	15	40	45
		Secondary			10	40	27	50
Ag 3	40nm Ag PVP	Primary			19	25	48	57
		Secondary			32	59	41	69
Ag 4	25nm Ag GA	Primary			15	13	36	37
		Secondary			27	79	39	75
Ag 5	6nm Ag GA	Primary			14	16	33	43
		Secondary			10	50	30	39
CeO_2 Bare	8nm CeO_2 Bare	Primary	49	55	48	53	79	90
		Secondary	61	90	70	95	88	98
CeO_2 Nanobyk	8nm CeO_2 Citrate	Primary	15	20	23	31	22	35
		Secondary	56	79	70	84	72	82
TiO2 NA	15nm Bare	Primary	60	68	61	69	60	74
		Secondary	81	94	82	96	86	98
TiO2 TINE	20nm Bare	Primary	70	72	70	74	70	75
		Secondary	80	91	82	95	84	97
ZnO Vive	20nm ZnO Na polyacrylate	Primary	25	38	30	39	30	37
		Secondary	20	95	25	76	26	28
ZnO TINE	30nm ZnO Bare	Primary	45	49	49	61	58	65
		Secondary	83	91	85	92	78	92
ZnO NAM	20nm ZnO Bare	Primary	46	47	49	59	58	65
		Secondary	85	91	85	91	83	90

Note: According to initial quantity and energy dissipated in reactors.
Source: Data from thesis research by L. Barton (DUKE University and Aix-Marseille University) (Barton et al., 2014a).

The distribution coefficients, which are a simple way of evaluating the quantities of "soluble" matter retained by a solid phase after a given contact time and with a given initial concentration (eq. 1)

$$\gamma = \frac{\text{Retained Nanomaterials (mg) / Bio-solids (mg)}}{\text{Nanomaterials in Supernatant (mg / L)}}$$

show that the behaviour is dependent on i) the presence of surface functionalisation, the possibility of reduction or oxidation leading to dissolution and solubilisation (Ag°, CeO_2) or even dissolution with a constant oxidation state (ZnO) compared to a chemically stable nanoparticle (TiO_2), ii) the contact time from 1 minute to 60 minutes in the oxidation reactor and the denitrification reactor (anaerobic). For example, Ag° particles measuring < 10 nm display gamma values which reduce over time in both reactors. This is due to faster dissolution kinetics than in the case of larger particles (Ma et al., 2012).

On the other hand, TiO_2 nanoparticles display a regular increase in γ over the contact time irrespective of the primary reactor (aerobic) or secondary reactor (anaerobic).

CeO_2 nanoparticles display γ values which regularly increase as the contact time increases and with high values due to the fact that reduction of cerium oxide remains low with contact time of less than 1 hour.

It is thus possible to differentiate between the nanoparticles which undergo rapid transformations depending both on their chemistry and their size, such as Ag° (Ma et al., 2012). Similarly, the presence of surface functionalisation enabled by organic molecules on the surface, which are used to mix these ENMs within a product, has a part to play with respect to their affinity for bioaggregates at least over short periods. A summary is provided in Box 5.3 below.

Box 5.3. **Summary of the use of retention, aggregation and sedimentation models**

A research paper by Barton et al. (2014b) provides initial predictions of the retention capacities of nanomaterials by bacterial aggregates. The distribution coefficient (γ), which is measurable from experiments, expresses the distribution of nanoparticles or nanomaterials between the aqueous phase where they are very mobile and the solid phase in the form of bacterial aggregates. The γ parameter, which can be subsequently derived mathematically, expresses the affinity of nanomaterials for bacteria present in the sludge. This affinity also depends on the affinity of soluble organic molecules present in the waste water which can adsorb onto nanomaterials and delay the retention onto bacteria. These affinities are also dependent on the chemical nature of the nanoparticles and the presence of surface functionalisation enabled by additional organic molecules on the surface of a product (these are frequently used to incorporate ENMs into cosmetics, plastics, etc.). This can also be modeled using the aggregation theory developed long ago and applied to water treatment using coagulation-flocculation, etc. (Thill et al., 1998).

What risks are involved in agricultural applications?

The vast majority of ENMs will be found in dried and composted sludge. These solid phases will in some cases be used as fertilisers in agriculture. The rare studies which do exist are either data from models showing transfer to surface water (Blaser et al., 2008), or laboratory research concerning the effects on plants or terrestrial organisms such as worms or bacteria in the rhizosphere. A recent paper demonstrates the stability of Ag_2S when composted (Lombi et al., 2013). However, the one criticism which can be made is that it appears that these tests have never been carried out with products containing ENMs and transformed under real-life conditions, thus releasing complex ENMs. Similarly, the rare studies are conducted outside real-life conditions, i.e. wastewater which has undergone all stages of the treatment process and generates sludge for composting containing ENMs, whether transformed or not. We have already seen that transformations within sewage treatment plants are important for ENMs such as ZnO, Ag°, CeO_2, CuO, etc., but not of course for TiO_2. Indeed, the mobility of these products which have been transformed within the treatment plant, their potential transformations in soil after application and interactions with plants and bacteria in the rhizosphere, along with transfer to surface water, have never been studied in depth.

Current research overview: location of teams involved in this field throughout the world

There are very few teams throughout the world investigating the efficiency of biological treatment of wastewater containing ENMs. In Europe, these are based in Great Britain, France and Switzerland for the most part. Teams in Switzerland and France take a similar approach to studying the mechanism associated with transformations in greater depth.

There is also the US consortium CEINT, which works alongside with France (GDRI I-CEINT, Labex SERENADE), and also with researchers in the United Kingdom, Austria, and others (the TINE – Transatlantic Initiative for Nanotechnology and the Environment – project). This US-backed project aims to assess transformations and the impact on processes involving nanomaterials which are present in an urban sewage treatment plant, as well as the effects on terrestrial organisms and plants. Nevertheless, this approach does not anticipate the direct use of composted sludge containing nanomaterials which has been treated in a sewage treatment plant.

A project by I-CEINT (France-USA) seeks to assess the impact and transfer of the nanomaterials present in sludge from sewage treatment plants whilst considering i) dispersivity and transfer to surface water by using CEINT mesocosms, ii) quantifying phyto-availability with respect to plants intended for human consumption, and iii) quantifying the direct and indirect effects of application with respect to bacterial communities in the rhizosphere.

Finally, teams throughout the world are working on the effects of nanomaterials on the diverse range of bacterial communities both in aerobic and anaerobic reactors. The latter are subject to particular attention in that they represent an essential stage in preparing the final material, especially for agricultural applications.

What research still needs to be carried out?

Current state of knowledge

The current state of knowledge can be summarised as follows:

1. Chemical transformations in sewage treatment plants, such as solubilisation by reduction or oxidation are important parameters to be taken into consideration in nanometric material balances. Widespread surface functionalisation by introducing nanoparticles into common products may slow down these transformations and maintain the initial oxidation or reduction state for longer by limiting contact with bacterial aggregates.
2. Work on the operation of the various treatment stages is still in its early stages and requires a more systematic approach to the development of bacterial communities in aerobic and anaerobic reactors according to nanomaterials' doses and their surface formulation. Experiments involving high concentrations appear to be of limited credibility.
3. Initial predictions of the retention capacities of nanomaterials by bacterial aggregates can be made by the distribution coefficient ( ) expressing the affinity of nanoparticles or nanomaterials between the aqueous phase and bacterial aggregates.
4. The mobility of ENMs which have been transformed within the treatment plant, their potential transformations in soil after application and interactions with plants and bacteria in the rhizosphere, along with transfer to surface water, have never been studied in depth.

Areas for further research

Current research often involves the use of activated sludge reactors; the anaerobic stage has not yet been fully explored. It also involves non-functionalised nanoparticles, whereas they are all surface-functionalised in consumer products (cosmetics, plastics, agri-foods, clothing, paint, etc.). There has been no research on the deterioration of products containing ENMs and studies on surface changes in nanoparticles in a sewage treatment plant do not exist. In order to remedy this, it seems essential to:

1. Use sufficiently large pilot plants incorporating all the relevant stages so that data can be extrapolated to a full-scale plant.
2. Work with the residues of various products, obtained in a reproducible manner (see the European NEPHH programme, for example) but which are widely used: cosmetics, paint, agri-foods, etc. under realistic conditions, which thus enable to monitor the changes in ENMs from the point at which they are discharged into water (well diluted) and at the different treatment stages in the plant. Studies have been conducted on changes in surface functionalisation of cosmetics (Botta et al., 2011; Labille et al., 2010; Auffan et al., 2009a, 2009b, 2010 etc.) under mild conditions and of Nanobyk (CeO_2 formulated with citrate molecules) in an aerobic reactor and a laboratory pilot (Barton et al., 2013). Such research is still very limited.
3. Assess the impact of agricultural sludge application and develop a similar test to the RHIZOtest, for example, which assesses the risks of metals being transferred to plants (ADAME, 2007). These experiments will need to be performed with transformed sludge under conditions close to real-life conditions and not with high concentrations of nanomaterials. The use of isotope tracing for nanomaterials would be extremely useful when monitoring the transfer process. 3D visualisation tools such as X-ray nano and microtomography are still not widely used in laboratories, but allow heavy elements to be located in a variety of tissues (plants, living organisms, etc.) in relation to observable effects. Finally, work is needed with actual soils for which precise details are available on their texture and component types as a function of the kinds of tested cultures.

In all these methods, the interdisciplinary aspect is paramount. The effects on living organisms (plants, bacteria, etc.) cannot be studied without considering biological diversity, growth, etc., and having some knowledge of transformation and transfer mechanisms which are the preserve of physico-chemists and specialists in transfers in porous media.

References

ADEME (2007), “Bilan des flux de contaminants entrant sur les sols agricoles de France métropolitaine: Bilan qualitatif de la contamination par les éléments tracés métalliques et les composés tracés organiques et application quantitative pour les éléments (Assessment of contaminants entering the agricultural soils of mainland France: Qualitative assessment of the contamination by metal components and traces)”, Final Report, 2007, *www.ademe.fr/sites/default/files/assets/documents/57992_sogreah.pdf*.

ADEME (2004), “Production and management of sewage treatment plant sludge in France (2000-04)”, Syntheses related to the production and management of sludge from wastewater treatment plants in France, *http://paysdefayence.free.fr/epuration-eaux/boues_STEP_synthese.pdf*.

Arnaout C.L. and C.K. Gunsch (2012), “Impacts of Silver Nanoparticle Coating on the Nitrification Potential of Nitrosomonas Europaea”, *Environmental Science & Technology*, Vol. 46, pp. 5387-5395.

Auffan, M. et al. (2010a), "Inorganic Manufactured Nanoparticles: How Their Physicochemical Properties Influence Their Biological Effects in Aqueous Environments", *Nanomedicine*, Vol. 5, No. 6, pp. 999-1007.

Auffan, M. et al. (2010b), "Structural Degradation at the Surface of a TiO_2-Based Nanomaterial Used in Cosmetics", *Environmental Science & Technology*, Vol. 44, No. 7, pp. 2689-2694.

Auffan, M. et al. (2009a), "Chemical Stability of Metallic Nanoparticles: A Parameter Controlling Their Potential Toxicity in Vitro", *Environmental Pollution*, Vol.157, No. 4, pp. 1127-1133.

Auffan, M. et al. (2009b), "Towards a Definition of Inorganic Nanoparticles from an Environmental, Health and Safety Perspective", *Nature Nanotechnology*, Vol. 4, No. 10, pp. 634-641.

Barton, L.E. et al. (2014a), "Monte Carlo Simulations of the Transformation and Removal of Ag, TiO_2, and ZnO Nanoparticles in Wastewater Treatment and Land Application of Biosolids", *Science of the Total Environment*, Vol. 511, pp. 535-543.

Barton, L.E. et al. (2014b), "Theory and Methodology for determining Nanoparticle Affinity for Heteroaggregation in Environmental Matrices Using Batch Measurements", *Environmental Engineering Science*, Vol. 31, No. 7, pp. 421-427.

Barton, L.E. et al. (2013), "Transformation of pristine and citrate-functionalized CeO_2 nanoparticles in a laboratory-Scale activated sludge reactor", *Environmental Science and Technology*, Vol. 48, No. 13, pp. 7289-7296.

Blaser, S.A. et al. (2008), "Estimation of Cumulative Aquatic Exposure and Risk Due to Silver: Contribution of Nano-Functionalized Plastics and Textiles", *Science of the Total Environment*, Vol. 390, No. 2-3, pp. 396-409.

Botta, C. et al. (2011), "TiO_2-Based Nanoparticles Released in Water from Commercialized Sunscreens in a Life-Cycle Perspective: Structures and Quantities", *Environmental Pollution*, Vol. 159, No. 6, pp. 1543-1548.

Brar, S.K. et al. (2010), "Engineered Nanoparticles in Wastewater and Wastewater Sludge", *Waste Management*, Vol. 30, pp. 504-520.

Doolette, C.L. et al. (2013), "Transformation of PVP Coated Silver Nanoparticles in Simulated Wastewater Treatment Processes and the Effect on Microbial Communities", *Chemistry Central Journal*, Vol. 7, No. 46, pp. 2-18.

Ganesh, R. et al. (2011), "Evaluation of Nanocopper Removal and Toxicity in Municipal Wastewaters", *Environmental Science and Technology*, Vol. 44, No. 20, pp. 7808-7813.

Gomez-Rivera, F. et al. (2012), "Fate of Cerium Dioxide (CeO2) Nanoparticles in Municipal Wastewater during Activated Sludge Treatment", *Bioresource Technology*, Vol. 108, pp. 300-304.

Jarvie, H.P. et al. (2009), "Fate of Silica Nanoparticles in Simulated Primary Wastewater Treatment", *Environmental Science and Technology*, Vol. 43, No. 22, pp. 8622-8628.

Kaegi, R. et al. (2011), "Behavior of Metallic Silver Nanoparticles in a Pilot Wastewater Treatment Plant", *Environmental Science and Technology*, Vol. 45, No. 9, pp. 3902-3908.

Kim, B. et al. (2010), "Discovery and Characterization of Silver Sulfide Nanoparticles in Final Sewage Sludge Products", *Environmental Science & Technology*, Vol. 44, No. 19, pp. 7509-7514.

Kiser, M.A. et al. (2010), "Biosorption of Nanoparticles to Heterotrophic Wastewater Biomass," *Water Research*, Vol. 44, No. 14, pp. 4105-4114.

Kiser, M.A. et al. (2009), "Titanium Nanomaterial Removal and Release from Wastewater Treatment Plants", *Environmental Science and Technology*, Vol. 43, No. 17, pp. 6757-6763.

Labille, J. et al. (2010), "Aging of TiO2 Nanocomposites Used in Sunscreen Creams. Dispersion and Fate of the Byproducts in Aqueous Environment", *Environmental Pollution*, Vol. 158, pp. 3482-3489.

Levard, C. et al. (2012), "Environmental Transformations of Silver Nanoparticles: Impact on Stability and Toxicity", *Environmental Science and Technology*, Vol. 46, pp. 6900-6914.

Levard, C. et al. (2011), "Sulfidation Processes of PVP-Coated Silver Nanoparticles in Aqueous Solution – Impact on Dissolution Rate", *Environmental Science and Technology*, Vol. 45, pp. 5260-5266.

Liang, Z. et al. (2010), "Bacterial Response to a Shock Load of Nanosilver in an Activated Sludge Treatment System", *Water Research*, Vol. 44, No. 4, pp. 5432-5438.

Limbach, K. et al. (2008), “Removal of Oxide Nanoparticles in a Model Waste Water Treatment Plant: Influence of Agglomeration and Surfactants on Clearing Efficiency”, *Environmental Science and Technology*, Vol. 42, pp. 5828-5833.

Liu, G. et al. (2011), “Effect of ZnO Particles on Activated Sludge: Role of Particle Dissolution”, *Science of the Total Environment*, Vol. 409, No. 14, pp. 2852-2857.

Lombi, E. et al. (2012), “Fate of Zinc Oxide Nanoparticles During Anaerobic Digestion of Wastewater and Post-treatment Processing of Sewage Sludge”, *Environmental Science and Technology*, Vol. 46, No. 16, pp. 9089-9096.

Luongo, L.A. and X. J. Zhang (2010), “Toxicity of Carbon Nanotubes to the Activated Sludge Process”, *Journal of Hazardous Materials*, Vol. 178, pp. 356-362.

Ma, R. et al. (2012), “Size-Controlled Dissolution of Organic-Coated Silver Nanoparticles”, *Environmental Science and Technology*, Vol. 46, No. 2, pp. 752-759.

Schmid, M. et al. (2003), “Characterization of Activated Sludge Flocs by Confocal Laser Scanning Microscopy and Image Analysis”, *Water Research*, Vol. 20, No. 2, pp. 2043-2052.

Snidaro, D. et al. (1997), “Characterization of Activated Sludge Flocs Structure”, *Water Science and Technology*, Vol. 36, No. 4, pp. 313-320.

Thill, A. et al. (2006), “Cytotoxicity of CeO2 Nanoparticles for Escherichia Coli – Physico-Chemical Insight of the Cytotoxicity Mechanism”, *Environmental Science & Technology*, Vol. 40, No. 19, pp. 6151-6156.

Thill, A. et al. (1998), “Determination of Structure of Aggregates by Confocal Scanning Laser Microscopy”, *Journal of Colloid and Interface Science*, Vol. 204, No. 2, pp. 357-362.

Tiede, K. et al. (2010), “Application of Hydrodynamic Chromatography-ICP-MS to Investigate the Fate of Silver Nanoparticles in Activated Sludge”, *Journal of Analytical Atomic Spectrometry*, Vol. 25, No. 7, pp. 1149-1154.

US EPA (2009), “Targeted National Sewage Sludge Survey Sampling and Analysis Technical Report”, United States Environmental Protection Agency, Washington, DC, *www.epa.gov/waterscience/biosolids/tnsss-tech.pdf*.

Wang, Y. et al. (2012), “Fate and Biological Effects of Silver, Titanium Dioxide, and C60 (Fullerene) Nanomaterials during Simulated Wastewater Treatment Processes”, *Journal of Hazardous Materials*, Vol. 201-202, pp. 16-22.

Westerhoff, P. et al. (2013), “Nanomaterial Removal and Transformation during Biological Wastewater Treatment”, *Environmental Engineering Science*, Vol. 30, No. 3, pp. 109-120.

Yang, Y. et al. (2013), “Impact of Metallic and Metal Oxide Nanoparticles on Wastewater Treatment and Anaerobic Digestion”, *Environmental Science: Processes and Impacts*, Vol. 15, pp. 39-48.

Yang, Y. et al. (2012), “Potential Nanosilver Impact on Anaerobic Digestion at Moderate Silver Concentrations”, *Water Research*, Vol. 46, pp. 1176-1184.

Zeyons, O. et al. (2009), “Direct and Indirect CeO2 Nanoparticles Toxicity for Escherichia Coli and Synechocystis”, *Nanotoxicology*, Vol. 3, No. 4, pp. 284-295.

Glossary

Aerobic process

A process in wastewater treatment that utilises biological treatment through aerobic transformation, i.e. reactions occurring in the presence of molecular oxygen, of micro-organisms in activated sludge. The bacterial development through air addition is used to adsorb (absorb) metallic elements and to aggregate particles to remove them from the effluent.

Source: OECD (2008), Test No. 314: Simulation Tests to Assess the Biodegradability of Chemicals Discharged in Wastewater, OECD Guidelines for the Testing of Chemicals, Section 3, OECD Publishing, Paris, *http://dx.doi.org/10.1787/9789264067493-en*.

Absorption / Adsorption

See sorption.

Anaerobic process

A process in wastewater treatment that utilises anaerobic transformation, i.e. reactions occurring under exclusion of molecular oxygen, for sludge digestion. The process stabilises the organic matter in activated sludge and reduces its toxicity by blocking metals and pathogens.

Source: OECD (2008), Test No. 314: Simulation Tests to Assess the Biodegradability of Chemicals Discharged in Wastewater, OECD Guidelines for the Testing of Chemicals, Section 3, OECD Publishing, Paris, *http://dx.doi.org/10.1787/9789264067493-en*.

Anoxic condition

Anoxic refers to the presence of combined oxygen (nitrate and nitrite) and the absence of free or dissolved oxygen. It is distinguished from anaerobic conditions where combined oxygen (nitrate and nitrite) and dissolved oxygen are totally excluded.

Source: Jeyanayagam, S (2005), "True confessions of the biological nutrient removal process", Florida water resources journal, January, pp. 37-46.

Best available techniques / technologies (BAT)

BAT is the realistically available state-of-the-art processes or facilities to suppress the emission of pollutants to the environment.). The definition of BAT in Europe refers to the European Directive 2010/75/EU: "best available techniques means the most effective and advanced stage in the development of activities and their methods of operation which indicates the practical suitability of particular techniques for providing the basis for emission limit values and other permit conditions designed to prevent and, where that is not practicable, to reduce emissions and the impact on the environment as a whole".

Source: EU (2010), "Directive 2010/75/EU of the European Parliament and of the Council of 24 November 2010 on industrial emissions (integrated pollution prevention and control)", *Official Journal of the European Union*, L 334/17, *http://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32010L0075&from=EN*.

Bottom ash

Bottom ash is the solid residual of waste material combustion in incineration plants.

Bioavailability

Bioavailability (or biological availability) means the extent to which a substance is taken up by an organism and distributed to an area within the organism. It is dependent upon physical-chemical properties of the substance, anatomy and physiology of the organism, pharmacokinetics, and route of exposure. Availability is not a prerequisite for bioavailability. An alternative definition for bioavailability is the rate and extent to which a substance can be taken up by an organism and is available for metabolism or interaction with biologically significant receptors. Bioavailability (biological availability) involves both release from a medium (if present) and absorption by an organism.

Source: United Nations (2013), “Globally Harmonised System of Classification and Labelling of Chemicals, Fifth revised edition”, United Nations Economic Commission for Europe, *www.unece.org/trans/danger/publi/ghs/ghs_rev05/05files_e.html*.

IPCS (2004), *IPCS Risk Assessment Terminology, Part 1: IPCS/OECD Key Generic Terms used in Chemical Hazard/Risk Assessment*, International Programme on Chemical Safety, World Health Organization, Geneva, *www.inchem.org/documents/harmproj/harmproj/harmproj1.pdf*.

Denitrification process

Denitrification is a process in wastewater treatment to remove nitrogen from effluents in order to avoid discharge of these nutrients and pollutants to surface water.

Source: OECD Environmental Outlook to 2050 (2012).

Ecotoxic

According to the Basel Convention, Annex III, the hazard characteristic H12”Ecotoxic” is defined as: Substances or wastes which, if released, present or may present immediate or delayed adverse impacts to the environment by means of bioaccumulation and/or toxic effects upon biotic systems. The ecotoxicological impact of a chemical substance or waste depends on the ability of the chemical substance or waste to act toxically on organisms in the environment as well as on the exposure of these organisms.

Source: UNEP (2003), *Interim guidelines on the hazardous characteristic H12-Ecotoxic*, Secretariat of the Basel Convention, Châtelaine, Switzerland, *http://archive.basel.int/meetings/sbc/workdoc/techgh12-e.pdf*.

Engineered nanomaterials (ENMs)

Nanomaterial designed for a specific purpose or function. Engineered nanomaterials (ENMs) and manufactured nanomaterials (MNMs) are used synonymously in various research documents. This publication will refer to ENMs for the purpose to align with ISO standards.

Source: ISO (2015), *Nanotechnologies – Vocabulary – Part 1: Core terms*, ISO/TS 80004-1:2015, International Organization for Standardization.

ISO (2012), *Nanotechnologies – Occupational risk management applied to engineered nanomaterials – Part 1: Principles and approaches*, ISO/TS 12901-1:2012, International Organization for Standardization.

Flue gas

Flue gas is the exhaust gas that is created through waste material combustion in incineration plants.

Fly ash

Fly ash is the residual particles of waste material combustion in incineration plants that ascend with flue gas.

Hazardous waste

Hazardous wastes are wastes that, owing to their toxic, infectious, radioactive or flammable properties pose a substantial actual or potential hazard to the health of humans and other living organisms and the environment.

Source: OECD (2001) “Glossary of statistical terms”, *http://stats.oecd.org/glossary/*, (accessed on 22 October 2015).

Incineration

Incineration is the controlled burning of solid, liquid or gaseous waste materials at high temperatures.

Source: OECD (2001) “Glossary of statistical terms”, *http://stats.oecd.org/glossary/*, (accessed on 22 October 2015).

Landfill Leachate

The residual liquid that drains through the landfill, which is commonly collected through landfill liners in controlled landfills for further treatment.

Landfilling

Landfill refers to the final placement of waste in or on the land in a controlled or uncontrolled way according to different sanitary, environmental protection and other safety requirements.

Source: OECD (2005) “Glossary of statistical terms”, *http://stats.oecd.org/glossary/*, (accessed on 22 October 2015).

Manufactured nanomaterials (MNMs)

See engineered nanomaterials (ENMs).

Nanomaterials (NMs)

Material with any external dimension in the nanoscale, i.e. size range from approximately 1 to 100 nm, or having internal structure or surface structure in the nanoscale.

Source: ISO (2015), *Nanotechnologies – Vocabulary – Part 1: Core terms*, ISO/TS 80004-1:2015, International Organization for Standardization.

ISO (2012), *Nanotechnologies – Occupational risk management applied to engineered nanomaterials – Part 1: Principles and approaches*, ISO/TS 12901-1:2012, International Organization for Standardization.

Nanotechnology

Nanotechnology: application of scientific knowledge to manipulate and control matter in the nanoscale (size range from approximately 1 nm to 100 nm) in order to make use of size- and structure-dependent properties and phenomena, as distinct from those associated with individual atoms or molecules or with bulk materials.

Source: ISO (2015), *Nanotechnologies – Vocabulary – Part 1: Core terms*, ISO/TS 80004-1:2015, International Organization for Standardization.

OECD (2014), "Considerations in moving towards a statistical framework for nanotechnology, Findings from a working party on nanotechnology pilot survey of business activity in nanotechnology", OECD, Paris.

Recycling

Recycling is the processing and use of wastes in production and consumption processes, for example, melting of scrap iron so that it can be converted into new iron products.

Source: OECD (2005) "Glossary of statistical terms", *http://stats.oecd.org/glossary/*, (accessed on 22 October 2015).

Surface functionalisation / Surface functionalised nanomaterials

Surface functionalised nanomaterials refer to those that are covered with chemicals such as organic and/or mineral molecules on their surfaces to retain specific features for industrial and commercial applications. As an example some sunscreens contain TiO2 coated with an Al oxy-hydroxide layer in order to limit the production of ROS (Reactive Oxygen Species) and prevent organic polymer to link with the cream.

Solid waste

Solid waste is useless and sometimes hazardous material with low liquid content. Solid wastes include municipal garbage, industrial and commercial waste, sewage sludge, wastes resulting from agricultural and animal husbandry operations and other connected activities, demolition wastes and mining residues.

Source: OECD (2003) "Glossary of statistical terms", *http://stats.oecd.org/glossary/*, (accessed on 22 October 2015).

Sorption

In this report, the term "sorption" includes both processes of "absorption" and "adsorption" where a substance takes up another by the whole volume or by the surface respectively.

Waste containing nanomaterials (WCNMs)

The term "waste containing nanomaterials" means typical municipal solid waste, which includes commercial similar to domestic waste and household waste containing nanomaterial. The term "nanowaste" is used in the context of specific waste containing nanomaterials, generated by nanomaterial production or even preparations of products. WCNM can be generated during the use phase, during the repair of products or in particular the disposal of products at the end of their lifecycle.

Waste management

Waste management includes the management of disposal, (which includes both permanent and temporary storage) and recovery of wastes, including subsequent disposal of residues from recovery operations. Waste collection is also considered an integral part of waste management.

Source: OECD (2007), Guidance Manual on Environmentally Sound Management of Waste, OECD Publishing, Paris, *http://dx.doi.org/10.1787/9789264042049-en*.

Wastewater sludge

Residual sludge from water purification plants and waste water treatment plants.

Wastewater treatment

Wastewater treatment is a process of collecting and treating wastewater through public sewage networks and wastewater treatment plants. The process can be sub divided into primary, secondary and/or tertiary sewage treatment:

Primary treatment: physical and/or chemical process involving settlement of suspended solids, or other process in which the Biological Oxygen Demand (BOD) of the incoming wastewater is reduced by at least 20% before discharge and the total suspended solids are reduced by at least 50%.

Secondary treatment: process generally involving biological treatment with a secondary settlement or other process, with a BOD removal of at least 70% and a Chemical Oxygen Demand (COD) removal of at least 75%.

Tertiary treatment: treatment of nitrogen and/or phosphorous and/or any other pollutant affecting the quality or a specific use of water (microbiological pollution, colour, etc.).

Source: OECD (2013), Environment at a Glance 2013: OECD Indicators, OECD Publishing, Paris, *http://dx.doi.org/10.1787/9789264185715-en*.

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

The OECD is a unique forum where governments work together to address the economic, social and environmental challenges of globalisation. The OECD is also at the forefront of efforts to understand and to help governments respond to new developments and concerns, such as corporate governance, the information economy and the challenges of an ageing population. The Organisation provides a setting where governments can compare policy experiences, seek answers to common problems, identify good practice and work to co-ordinate domestic and international policies.

The OECD member countries are: Australia, Austria, Belgium, Canada, Chile, the Czech Republic, Denmark, Estonia, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Israel, Italy, Japan, Korea, Luxembourg, Mexico, the Netherlands, New Zealand, Norway, Poland, Portugal, the Slovak Republic, Slovenia, Spain, Sweden, Switzerland, Turkey, the United Kingdom and the United States. The European Union takes part in the work of the OECD.

OECD Publishing disseminates widely the results of the Organisation's statistics gathering and research on economic, social and environmental issues, as well as the conventions, guidelines and standards agreed by its members.

OECD PUBLISHING, 2, rue André-Pascal, 75775 PARIS CEDEX 16
(97 2015 16 1 P) ISBN 978-92-64-24061-2 – 2016

Nanomaterials in Waste Streams

CURRENT KNOWLEDGE ON RISKS AND IMPACTS

Contents

Consult this publication on line at ***http://dx.doi.org/10.1787/9789264249752-en.***

This work is published on the OECD iLibrary, which gathers all OECD books, periodicals and statistical databases.
Visit ***www.oecd-ilibrary.org*** for more information.

OECD*publishing*
www.oecd.org/publishing

ISBN 978-92-64-24061-2
97 2015 16 1 P

9 789264 240612